PATENT ABSTRACTS OF JAPAN

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(54) ANTI-FOGGING MIRROR FOR BATHROOM

(57)Abstract:
PROBLEM TO BE SOLVED: To repeatedly reproduce a highly hydrophilic surface with a simple cleaning means and to maintain excellent anti-fogging and antifouling properties over a long period in the anti-fogging mirror for a bathroom by imparting specified values to the average height, the average width and the center line average surface roughness respectively in a layer surface composed of a hydrophilic inorganic oxide.
SOLUTION: A layer composed of a hydrophilic inorganic oxide is formed on a substrate surface. A projecting and recessing structure with average height and average width of respectively 0.4-200 nm and 0.1-50 nm center line average surface roughness Ra at an arbitrary position of the substrate surface measured with an atomic force microscope for the layer surface is formed. The method for forming projecting and recessing parts on the substrate surface is optionally selected from well-known methods. A method for forming a film with fine projecting and recessing parts on the substrate surface such as a sol coating method, a plating method, a CVD method, a sputtering method or a vacuum deposition method, a method for directly forming projecting and recessing parts on the substrate such as a sandblast method or an etching method and a method for forming fine projecting and recessing parts on a forming mold and transferring them to the substrate are mentioned.

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CLAIMS

[Claim(s)]

[Claim 1] It is the fog resistance mirror for bathrooms in which the layer which consists of a hydrophilic inorganic oxide is formed in the rear face on the mirror front face which gave the reflective coat, and the concavo-convex average height and the average width of face in the location of the arbitration on the front face of a base material which measured said layer front face with the atomic force microscope are 0.4nm or more 200nm or less, and it is characterized by having the concavo-convex structure where center line average surface roughness Ra is 0.1nm or more 50nm or less.

[Claim 2] The fog resistance mirror for bathrooms according to claim 1 in which the average height of the concavo-convex structure measured with the atomic force microscope in the location of the arbitration of the front face of said layer is 0.8nm or more 40nm or less, and 9nmor more 100nm or less and center line average surface roughness Ra are characterized by 0.1nm or more being 10nm or less by average width of face.

[Claim 3] The fog resistance mirror for bathrooms according to claim 1 to 2 characterized by including a silicic-acid alkali-metal salt in said hydrophilic inorganic oxide layer.

[Claim 4] Said concavo-convex structure is a fog resistance mirror for bathrooms according to claim 1 to 3 characterized by being fractal structure.

[Claim 5] The fog resistance mirror for bathrooms according to claim 1 to 4 characterized by the thickness of said layer being 400nm or less.
[Claim 6] Said metallic oxide is a fog resistance mirror for bathrooms according to claim 1 to 5 characterized by being one or more sorts chosen from the group which consists of a silica, an alumina, a zirconia, a titania, tin oxide, and a zinc oxide.
[Claim 7] It is the fog resistance mirror for bathrooms according to claim 6 characterized by a zirconia, a titania, the tin oxide, and a zinc oxide being photocatalysts among said metallic oxides.
[Claim 8] Said layer is a fog resistance mirror for bathrooms according to claim 1 to 7 characterized by forming by the sol applying method.
[Claim 9] Said layer is a fog resistance mirror for bathrooms according to claim 1 to 7 characterized by forming by the chemical etching method.
[Claim 10] Said layer is a fog resistance mirror for bathrooms according to claim 1 to 7 characterized by forming with a vacuum deposition method.
[Claim 11] Said layer is a fog resistance mirror for bathrooms according to claim 1 to 7 characterized by forming by the sputtering method.
[Claim 12] Said layer is a fog resistance mirror for bathrooms according to claim 1 to 7 characterized by forming with a CVD method.
[Claim 13] The fog-resistance mirror for bathrooms in which it is the antifog mirror for bathrooms equipped with the hydrophilic front face, and the concavo-convex average height and the average width of face in the location of the arbitration on said front face of a layer which is equipped with the layer which has said concavo-convex structure, and the layer which uses a silicic-acid alkali-metal salt as a principal component on said layer further, and was measured with the atomic force microscope are 0.4nm or more 200nm or less, and center line average surface-roughness Ra is characterized by to 0.1nm or more be 50nm or less.
[Claim 14] The fog resistance mirror for bathrooms according to claim 13 in which 0.8nm or more 40nm or less and average width of face are characterized [the average height of the irregularity on said front face of a layer] by 0.1nm or more being 10nm or less by 9nmor more 100nm or less and center line average surface roughness Ra.
[Claim 15] The fog resistance mirror for bathrooms according to claim 1 to 14 in which F-potential on the front face of a mirror is characterized by being negative in underwater [of the pH7 neighborhood].
[Claim 16] The fog resistance mirror for bathrooms according to claim 1 to 15 characterized by an angle of sweepback with water [in / in said mirror / an elevation surface] having the hydrophilic property of 20 or less degrees.
[Claim 17] The fog resistance mirror for bathrooms according to claim 1 to 16 characterized by containing the matter with which said mirror has antibacterial.
[Claim 18] The fog resistance mirror for bathrooms according to claim 1 to 17 which is said mirror for bathrooms and is characterized by presenting antifouling property, fog resistance, waterdrop formation tightness, and/or waterdrop adhesion tightness over the whole surface by forming the water screen in this mirror plane with the water concerning a mirror plane, or the steam which contacts.

[Translation done.]
* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] The amount of contamination addition of this invention of dirt is large, and it relates mainly to the hydrophilic antifog mirror for bathrooms which was excellent in the fog resistance which can be suitably used in a bathroom, a shower room, etc., dripproofness, antifouling property, and self-consecration nature under the environment which a lot of [continuously] steams and water require.
[0002]
[Description of the Prior Art] As an approach of preventing the cloudiness and dirt of a bathroom mirror, giving a hydrophilic property to a mirror front face is performed conventionally. The approach of applying hydrophilic matter which applies a surfactant to a mirror front face, such as an approach and a hydrophilic monomer polymer, as an approach of giving a hydrophilic property etc. is learned. By water-screen-izing the waterdrop which adhered to the front face with the surfactant, by absorbing water the moisture adhering to a mirror front face, adhesion and formation of waterdrop are prevented and, according to the approach of applying a hydrophilic monomer polymer etc., it becomes possible to prevent the cloudiness and dirt on the front face of a member according to the approach of applying a surfactant. Moreover, once it pours water on the mirror front face produced using the obscured glass which put the countless crack into the longitudinal direction and formed irregularity parallel to a front face in JP,7-236553,A, when a front face turns into a flat surface with the water which entered the crevice, it becomes transparent and blooming cloudy by the water screen and preventing is indicated.
[0003]
[Problem(s) to be Solved by the Invention] A surfactant and the hydrophilic matter tend to flow and fall off with moisture, and a problem has water in the durability of effect in this environment frequently like especially a bathroom. Moreover, if a hydrophilic monomer polymer absorbs water, a front face will become easy to get damaged softly. In using in the environment where the vapor pressure under an operating environment is high, like a bathroom especially, a coefficient of water absorption increases and the inclination becomes very remarkable. Furthermore, both the surfactant and the hydrophilic monomer polymer had the fault of being easy to adsorb the dirt in air etc. As for a bathroom, the cleaning agent used at the time of a shampoo and body washing besides being dirt, soap, **, sebum resulting from the metal ion in tap water, etc. especially the silicon oil which is also a moisturizing component in a rinse, the cation system surfactant for obtaining admiration smoothly, etc. especially have very many contaminations from which a mirror front face is changed to the property which becomes

easy to crawl water by adhering to a mirror front face. Furthermore, they disperse directly at the time of a shampoo and body washing, disperse indirectly with a shower, or are in the situation of being easy to adhere. Moreover, in the bath interior of a room, by the part with especially irregularity, a microorganism tends to breed, a microorganism breeds on the mirror front face which gave irregularity, and a hydrophilic property may be prevented from moisture and the organic substance being abundance. thus, the environment where a variety of [a bathroom environment] dirt exists, and tends to adhere and where a contamination load is large -- it is -- in addition -- and since it is the environment which applies water frequently, it was that the above-mentioned mirror can demonstrate fog resistance and antifouling property, only while being able to hold the condition with an early pure mirror, and it cannot almost hold fog resistance and antifouling property for a long period of time

[0004] For a reason [more than / this invention], by the simple defecation approach of extent on which water is poured with the shower which was the difficulty of implementation, a hydrophilic advanced front face is repeated, and it reappears, and aims at offering the hydrophilic antifog mirror for bathrooms which can maintain good antifog and antifouling property over a long period of time.

[0005]

[Means for Solving the Problem] It is made for 0.4nmor more 200nm or less and center line average surface roughness Ra to have the concavo-convex structure where the concavo-convex height and the width of face in the location of the arbitration on the front face of a base material which the layer which consists of a hydrophilic inorganic oxide is formed in the base material front face that this invention should solve the above-mentioned technical problem, and was measured with the atomic force microscope on said front face of a layer are 0.1nm or more 50nm or less formed. It may be concavo-convex average height of 40nm or less of 0.8nm or more, concavo-convex average width of face of 100nm or less of 9nm or more, and less than [more than center line average surface roughness Ra0.1nm10nm] more preferably. It is transparent by forming in a base material front face the layer which consists of a hydrophilic inorganic oxide, and forming such concavo-convex structure in a layer front face, and the following functions are demonstrated, without spoiling the texture of a base material.

(1) Since a hydrophilic side is fractal-structure (structure where a fractal dimension is 2.01-2.99 dimensions), it comes to present an advanced hydrophilic property. Therefore, an attached groundwater drop is water-screen-ized uniformly. Thereby, sufficient cloudy tightness is demonstrated also in the use in bathroom space with many steams.

(2) The water screen will be formed in a front face, if water is beforehand poured with the shower etc. just before use in order to present an advanced hydrophilic property. If this water screen exists, since a mirror front face excels a dirt component in the compatibility over water far, antifouling property will be demonstrated also in bathroom space with many dirt burdens. In bathroom space, since it is convenient even if a floor gets wet with water, it is available in this property, and only by pouring water with the shower etc. beforehand just before use each time at the long period of time, it continues at a long period of time, and prevention of not only fog resistance but the visibility fall by adhesion of soap etc. is attained in the time of use. Moreover, it is washed away by the shower which also mentioned above the dirt in the air which adhered at the time of un-using it.

(3) Since concavo-convex structure is very detailed, the bacillus or mold which are easy

to inhabit a bathroom cannot enter into irregularity. Therefore, the dirt by the bacillus or mold is also prevented.
(4) Since the hard layer which consists of an inorganic oxide is formed, a mirror front face cannot get damaged easily. Therefore, the fall of the visibility of the mirror by generating of a blemish can be prevented. It can ask for the height of the irregularity on the front face of a base material, width of face, and surface roughness using an atomic force microscope. Since the gas which entered the surface water of adsorption and a front face cannot interfere and an exact value cannot be known with the surface roughness plan of a contact process in case a complicated and detailed concavo-convex front face is measured, measuring using an atomic force microscope is desirable. As for concavo-convex height and width of face, it is desirable to carry out to 1/2 or less of the wavelength of the light, i.e., 200nm. It is because coloring of the surface layer by interference of light can be prevented and texture of a base material is not spoiled. Moreover, as for concavo-convex height and width of face, it is desirable that it is 0.4nm or more. It is because sufficient mechanical reinforcement is securable. Surface roughness is mainly decided by concavo-convex height, and is set to surface roughness (Ra) = height / 4 in the cross section of the typical front face shown in drawing 1. Since it is desirable here that concavo-convex height is 0.4nm or more 200nm or less, 0.1nm or more 50nm or less of surface roughness is desirable.
[0006] In this invention, the fog resistance mirror for bathrooms characterized by including a silicic-acid alkali-metal salt in the hydrophilic inorganic oxide layer of said concavo-convex structure is offered further that the above-mentioned technical problem should be solved. According to this, by controlling the property to begin to melt gradually, self-consecration of the mirror front face is carried out over a long period of time, fixing of dirt is prevented without applying time and effort, and a pure and hydrophilic advanced front face is repeated simple, it reappears, and good antifog and antifouling property are made maintainable over a long period of time.
[0007] In this invention, the hydrophilic composite further characterized by said concavo-convex structure being fractal structure that the above-mentioned technical problem should be solved is offered. Fractal structure is multistage concavo-convex structure which includes the concavo-convex structure of a small period in the concavo-convex structure and structure of a large period on the surface of a base material. By carrying out to fractal structure, i.e., the complicated structure which has still finer irregularity in irregularity, the water holding capacity on the front face of a base material is heightened, and it becomes possible to make a still more advanced hydrophilic property discover.
[0008] In the desirable mode of this invention, said base material is formed by chemical etching. According to chemical etching, a clear reflected image without a twin image is acquired.
[0009] In the desirable mode of this invention, said base material is formed by warm water immersion. in order not to use a drug solution etc. according to warm water immersion -- safe -- in addition -- and irregularity can be formed simple.
[0010] Said base material is equipped with the layer containing one or more sorts of a metallic oxide joined to a base material front face in the desirable mode of this invention. By making one or more sorts of metallic oxides contain, the irregularity of the request which presents an advanced hydrophilic property can be formed easily.
[0011] It is made for the thickness of said layer to be set to 400nm or less in the desirable

mode of this invention. By considering as said thickness, the transparent film without an optical interference which has the outstanding fog resistance, or nebula can be formed.
[0012] In the desirable mode of this invention, said layer is formed by the sol applying method. According to the sol applying method, with the magnitude of a base material, and a configuration, since the constraint on a facility is not received, a special facility cannot be required but coat formation can be carried out on a base material front face simple.
[0013] In the desirable mode of this invention, said layer is formed with vacuum deposition. According to vacuum deposition, it is not based on the class of base material, and the class of oxide to be used, but it is uniform and the transparent film which has the outstanding fog resistance can be formed.
[0014] In the desirable mode of this invention, said layer is formed by sputtering. According to sputtering, the uniform and firm film can be formed.
[0015] In the desirable mode of this invention, said layer is formed by CVD. According to CVD, the better film of endurance can be formed.
[0016] In the desirable mode of this invention, a metallic oxide is chosen from the group which consists of a silica, an alumina, a zirconia, a titania, tin oxide, and a zinc oxide. By using these oxides, the hydrophilic advanced front face excellent in a water resisting property and chemical resistance is obtained. It is desirable to use what has a zirconia, a titania, the tin oxide, and the photocatalyst activity of a zinc oxide among these metallic oxides. By doing so, a much more advanced hydrophilic property can be acquired by the ultraviolet rays from indoor lighting and an indoor aperture.
[0017] In the desirable mode of this invention, **** was further formed for the silicic-acid alkali-metal salt as the principal component on the front face which has concavo-convex structure, the concavo-convex average height and the average width of face in the location of the arbitration of the outermost surface measured with the atomic force microscope are 0.4nm or more 200nm or less, and center line average surface roughness Ra is equipped with 0.1nm or more layer it is [layer] 50nm or less. It may be concavo-convex average height of 40nm or less of 0.8nm or more, concavo-convex average width of face of 100nm or less of 9nm or more, and less than [more than center line average surface roughness Ra0.1nm10nm] more preferably. A still better hydrophilic front face is obtained by forming irregularity further on the front face which formed irregularity beforehand. Moreover, even if an interference fringe and nebula are accepted, said front face cancels them and has the effectiveness made into transparence. Although it is not limited, in addition, surface concavo-convex structure is desirable, if structure according to claim 1 to 18 is made.
[0018] In the desirable mode of this invention, a concave convex layer is formed by the sol applying method. It is because the sol of a metallic oxide can obtain the thing of various particle diameter and description, so a suitable thing can be chosen according to the irregularity of the base material formed beforehand.
[0019] As for a concave convex layer, in the desirable mode of this invention, forming by sputtering is desirable. According to sputtering, the uniform and firm film can be formed.
[0020] In the desirable mode of this invention, a concave convex layer is formed by CVD. According to CVD, the better film of endurance can be formed.
[0021] As for the metallic oxide which forms a concave convex layer, in the desirable mode of this invention, it is desirable to choose out of the group which consists of a

silica, an alumina, a zirconia, a titania, tin oxide, and a zinc oxide. It is easy to obtain the good irregularity of a hydrophilic property by using these metallic oxides. It is desirable to use what has a zirconia, a titania, the tin oxide, and the photocatalyst activity of a zinc oxide among these metallic oxides. By doing so, a much more advanced hydrophilic property can be acquired by the ultraviolet rays from indoor lighting and an indoor aperture.

[0022] The 2-dimensional cross-section structure of a concavo-convex hole has the largest surface section, and it is made to be so narrow that it go to the back in the desirable mode of this invention. The surface section has the largest 2-dimensional cross-section structure of a hole, and if a configuration which is so narrow that it goes to the back is carried out, even if stained with dirt, it will be easy to fall, and it will become possible to maintain a good hydrophilic property.

[0023] It is made for an angle of sweepback with water [in / in said mirror / an elevation surface] to have the hydrophilic property of 20 or less degrees in the desirable mode of this invention. It is because the water which adhered to the mirror front face in the elevation surface shows drip nature and becomes easy to present antifouling property, fog resistance, waterdrop formation tightness, and waterdrop adhesion tightness over the whole mirror surface. Drip nature does not serve as waterdrop, when water is poured, but it means the condition of having formed the water screen in the mirror plane in elevation surfaces, such as a wall of a bathroom. Moreover, an angle of sweepback is a contact angle of the water when dipping and pulling up a sample in a tank with constant speed.

[0024] The matter which has antibacterial is supported by the outermost surface of composite in the desirable mode of this invention. Since the bacillus and microorganism which are one factor which checks a hydrophilic property by supporting the matter which has antibacterial can be annihilated or propagation can be controlled, a good hydrophilic property becomes maintainable.

[0025] In the desirable mode of this invention, underwater F-potential of pH7 near [a composite front face] is made negative. By making F-potential negative, when water contacts a mirror front face, disinfection and/or the antifouling effectiveness can be given. It is known that the dirt, the fungus, etc. of the circumference of water are generally charged in negative in underwater [of the pH7 neighborhood]. Therefore, by making negative F-potential on the front face of composite, where water is contacted, a composite front face, and dirt and a fungus can oppose electrically, and can prevent adhesion of dirt and a fungus.

[0026]

[Embodiment of the Invention] The fog resistance mirror of this invention can be suitably used mainly as a hydrophilic antifog mirror for bathrooms which was excellent in fog resistance, dripproofness, antifouling property, and self-consecration nature in the bathroom, the shower room, etc. under [of the circumference of water] the environment which the amount of contamination addition of dirt is especially large, and a lot of [continuously] steams and water require.

[0027] In this invention, as an approach of forming irregularity in a base material front face Although what is necessary is just to choose from the well-known approach instead of what is limited, the sol applying method, Like drawing 2 therefore by the approach of forming film which has detailed irregularity on a base material front face, such as the galvanizing method, a CVD method, sputtering, and a vacuum deposition method,

sandblasting, etching, etc. Like drawing 3 , there are an approach of forming direct irregularity in a base material, the approach of forming detailed irregularity on a die and imprinting irregularity to a base material, etc. After forming irregularity in a transparent base material front face, a reflective coat may be given and mirror-ized at the rear face, and irregularity may be formed after giving and mirror-izing a reflective coat at the rear face previously.

[0028] In this invention, silicic-acid sodium, a silicic-acid potassium, a silicic-acid lithium, and silicic-acid AMMOUMU can use suitably as a silicic-acid alkali-metal salt.

[0029] In this invention, it is desirable to form irregularity in a base material front face by chemical etching. Chemical etching is the approach make the steam which generates a base material when immersion or its solution is warmed in the solution of an acid, alkali, and a peroxide contact, and the chemical reaction performs surface treatment. As a solution to be used, water solutions, such as a hydrochloric acid, a sulfuric acid, an ammonium sulfide, fluoric acid, boron fluoride, and a silicofluoric acid, are mentioned.

[0030] In this invention, it is desirable to form irregularity in a base material front face by warm water immersion. in order not to use a drug solution etc. according to warm water immersion -- safe -- in addition -- and irregularity can be formed simple. Water may also be pure water or tap water anything. When the processing time is taken into consideration, 60 degrees C or more of water temperature are [that what is necessary is just 40 degrees C or more] desirable.

[0031] In this invention, it is desirable to carry out covering formation of the layer containing one or more sorts of a metallic oxide on a base material front face. According to this, the irregularity of the request which presents an advanced hydrophilic property can be formed easily. as the approach of carrying out covering formation of said oxide -- from well-known approaches, such as the sol applying method, vacuum deposition, sputtering, a CVD method, and the galvanizing method, -- you may choose -- moreover -- other than this . According to the sol applying method, with the magnitude of a base material, and a configuration, since the constraint on a facility is not received, a special facility cannot be required but it can carry out simple. According to a CVD method, sputtering, and vacuum deposition, although the application to a big base material receives constraint on a facility, it becomes possible [forming the uniform and stabilized thin film]. By making processing temperature high in these approaches, it is possible to raise more endurance, such as alkali resistance and warm water-proof nature.

[0032] It is made for the thickness of the coat of said oxide to be set to 400nm or less in this invention. When the coat which exceeds 400nm especially with one kind of oxide is formed, the interference fringe by interference of light, nebula, etc. occur, and it is easy to produce exterior fault. Moreover, if thickness becomes thick, abrasion resistance will fall, and becoming easy to attach a blemish is not avoided, either.

[0033] As a metallic oxide here A silica, an alumina, a zirconia, Seria, Yttria, BORONIA, a magnesia, calcia, a ferrite, hafnia, Titanium oxide, a zinc oxide, a tungstic trioxide, ferric oxide, a cuprous oxide, A cupric oxide, bismuth(III) oxide, the tin oxide, nickel oxide, cobalt oxide, Single oxides, such as barium oxide, a strontium oxide, and a vanadium oxide, Multiple oxides, such as barium titanate, a calcium silicate, water glass, an aluminosilicate, calcium phosphate, strontium titanate, potassium titanate, barium titanate, titanic-acid calcium, and aluminosilicate, can use suitably. Especially, it is desirable to use a silica, an alumina, a zirconia, a titania, the tin oxide, or a zinc oxide. A

silica and an alumina are good for forming small fine irregularity, and a zirconia, a titania, the tin oxide, and a zinc oxide are desirable for forming big irregularity. In the sol applying method, a silica with various available things is desirable about the description of particle diameter and the sol mentioned later. The silica is the cheapest and its practicality is very high. Moreover, an advanced hydrophilic property can be acquired by using the silica whose F-potential is negative, a zirconia, a titania, and the tin oxide in underwater [of the pH7 neighborhood]. It is using a desirable silica with the lowest surface potential, and a still more advanced hydrophilic property can be acquired by use of a silica.

[0034] As for a metallic-oxide particle, in this invention, it is desirable to consider as the gestalt of the sol which water or a hydrophilic solvent was made to distribute to colloid. Although it is not limited as long as make stability distribute said metallic oxide as a hydrophilic solvent, it makes homogeneity and a smooth coat form on a base material and it gets especially, as a desirable thing, the boiling point can mention an organic solvent 200 degrees C or less. As an example of a desirable organic solvent, a methanol, ethanol, n-propanol, Isopropanol, t-butanol, isobutanol, n-butanol, 2-methyl propanol, a pentanol, ethylene glycol, mono-acetone alcohol, Diacetone alcohol, ethylene glycol monomethyl ether, 4-hydroxy-4-methyl-2-pentanone, Dipropylene glycol, propylene glycol, tripropylene glycol, 1-ethoxy-2-propanol, 1-butoxy-2-propanol, 1-propoxy-2-propanol, propylene glycol monomethyl ether, Dipropylene glycol monomethyl ether, dipropylene glycol mono-ethyl ether, Ester solvents, such as hydrocarbon system solvents, such as alcohols solvents, such as tripropyllene glycol monomethyl ether and 2-butoxyethanol, and n-hexane, toluene, a xylene, a mineral spirit, methyl acetate, ethyl acetate, and butyl acetate, can be mentioned.

[0035] In this invention, when carrying out coat formation on a base material front face by the sol applying method, it is desirable to use the coating constituent made into a metallic oxide 0.05 - 20 weight sections, and a solvent 99.95 - 80 weight sections. By applying said coating liquid to a base material front face, it has the outstanding fog resistance and the transparent film without an optical interference or nebula can be formed.

[0036] Moreover, when based on the sol applying method, it is desirable to use the shape of feathers with a chain-like metallic oxide with a granular metallic oxide with a mean particle diameter of 1-100nm, a pitch diameter [of 1-50nm], and an average die length of 10-1000nm, a pitch diameter [of 1-50nm], and an average die length of 10-500nm or a cylindrical metallic oxide. As a granular metallic oxide with a mean particle diameter of 1-100nm, a silica, an alumina, etc. are mentioned as a chain-like metallic oxide with a pitch diameter [of 1-50nm], and an average die length of 10-1000nm, and a silica, a zirconia, etc. are mentioned for an alumina, a titania, etc. as the shape of feathers with a pitch diameter [of 1-50nm], and an average die length of 10-500nm, and a cylindrical metallic oxide. If the shape of the shape of a chain and feathers and a cylindrical metallic oxide are used, the endurance of the film formed in the base material front face can be raised. Moreover, if a granular inorganic oxide is used, after having desired irregularity, the film with more high smooth nature can be formed.

[0037] In this invention, it is desirable to make a base material surface layer contain the binder for fixing said metallic oxide to said base material front face. It is because the adhesion on the front face of a base material improves with a binder and still more

advanced endurance and abrasion resistance are obtained. As a binder, the binder of quality of organic, such as a binder of minerals, such as a cover coat, water glass, and silicone, thermosetting resin, a photo-setting resin, and thermoplastics, etc. can be used.
[0038] In this invention, a surfactant can be included in said coating liquid. As an example of the surface active agent which can be added, sulfonic-acid polyoxyethylene-alkyl-phenyl-ether ammonium salt, Sulfonic-acid polyoxyethylene-alkyl-phenyl-ether sodium salt, Fatty-acid potash soap, fatty-acid sodium soap, sodium dioctyl sulfosuccinate, Alkyl sulfate, alkyl ether sulfate, alkyl sulfate specific salt, Alkyl ether sulfate specific salt, polyoxyethylene-alkyl-ether sulfate, Polyoxyethylene-alkyl-ether sulfate specific salt, an alkyl sulfate TEA salt, A polyoxyethylene-alkyl-ether sulfate TEA salt, 2-ethylhexyl alkyl-sulfuric-acid ester sodium salt, Acyl methyl taurine acid sodium, lauroyl methyl taurine acid sodium, Sodium dodecylbenzenesulfonate, sulfo succinic-acid lauryl disodium, Polyoxyethylene sulfo succinic-acid lauryl disodium, polycarboxylic acid, TO me -- oil ZARUKOSHIN, AMIDOE-TERUSARUFE-TO, and lauroyl ZARUKOSHINE - Anionic surface active agents, such as sulfo FA ester sodium salt; Polyoxyethylene RAURIRUE-Tell, Polyoxyethylene TORIDESHIRUE-Tell, polyoxyethylene ASECHIRUE-Tell, Polyoxyethylene stearylether, polyoxyethylene OREIRUE-Tell, Polyoxyethylene alkyl ether, polyoxyethylene alkyl ester, The polyoxyethylene alkylphenol ether, polyoxyethylene nonyl phenyl ether, Polyoxyethylene octyl phenyl ether, polyoxyethylene RAURA-TO, Polyoxyethylene stearate, polyoxyethylene alkyl phenyl ether, Polyoxyethylene oleate, sorbitan alkyl ester, polyoxyethylene sorbitan alkyl ester, Polyether denaturation silicon, polyester denaturation silicon, sorbitan RAURA-TO, Sorbitan stearate, sorbitan palmitate, sorbitan sesquioleate, Sorbitan oleate, polyoxyethylene sorbitan RAURA-TO, Polyoxyethylene sorbitan stearate, polyoxyethylene sorbitan palmitate, Polyoxyethylene sorbitan oleate, glycero-RUSUTEARE-TO, Polyglyceryl fatty acid ester, alkyl ARUKIRO-RUAMIDO, lauric-acid diethanolamide, Oleic acid diethanolamide, an oxyethylene dodecyl amine, a polyoxyethylene dodecyl amine, Polyoxyethylene alkylamine, a polyoxyethylene octadecyl amine, Polyoxyethylene alkyl propylenediamine, polyoxyethylene oxypropylene block polymer, Nonionic surface active agents, such as polyoxyethylene stearate; A dimethyl alkyl betaine, Amphoteric surface active agents, such as an alkyl glycine, an amide betaine, and imidazoline; Octadecyl dimethylbenzyl ammoniumchloride, Alkyldimethyl benzyl ammoniumchloride, tetradecyl dimethylbenzyl ammoniumchloride, Dioleoyl dimethylannmonium chloride, the 4th class salt of 1-hydroxy-2-alkyl imidazoline, An alkyl iso quinolinium star's picture, a giant-molecule amine, octadecyl trimethylammonium chloride, Alkyl trimethylammonium chloride, dodecyl trimethylammonium chloride, Hexadecyl trimethylammonium chloride, behenyl trimethylammonium chloride, Cationic surfactants, such as the 4th class salt of alkyl imidazoline, dialkyl dimethylannmonium chloride, octadecyl amine acetate, tetradecylamine acetate, alkyl propylenediamine acetate, and JIDESHIRU dimethylannmonium chloride, etc. are mentioned.
[0039] In this invention, that what is necessary is just to choose suitably the approach of applying said coating liquid to a base material front face from a well-known approach, although the spray coating method using an air gun, an air loess gun, an aerosol spray, etc., a spin coating method, a DIP coating method, the flow coating method, the roll coating method, brush painting, sponge coating, etc. are raised, it is not limited to these.

Moreover, various shampoos, primers and a cleaning agent, compounds, an antistatic agent, etc. can also be used as processing before applying said coating liquid to a base material front face.
[0040] Which approach may be [that what is necessary is just to perform suitably heat treatment after applying coating liquid to a base material front face according to the class and property of coating liquid and a base material] used for air drying, heating, infrared radiation, UV irradiation, etc. A solvent may only be vaporized, it may dry and a request may also be good. Although a finishing agent is applied on the surface of goods and subsequently being heat-treated as an approach in the case of heat-treating, the count of spreading and heat treatment may be 2 times or more. After repeating only spreading two or more times, various approaches, such as heat-treating by once and performing a series of actuation of spreading and heat treatment two or more times, are mentioned.
[0041] In this invention, it is also possible to form the concave convex layer which consists of a metallic oxide further like drawing 4 on the base material front face which formed irregularity beforehand. Although what is necessary is just to choose from a well-known approach the irregularity formed beforehand, it is desirable to form by the sol applying method, the vacuum deposition method, sputtering, and CVD as mentioned above, and, as for the concavo-convex structure, it is desirable to go into the range of above-mentioned concavo-convex height, width of face, and surface roughness. As a metallic oxide which forms a concave convex layer, although what is necessary is just to choose from the above-mentioned metallic oxides, it is desirable to use a silica, an alumina, a zirconia, a titania, the tin oxide, and a zinc oxide especially. It is desirable to use what has photocatalyst activity, such as a zirconia, a titania, tin oxide, and a zinc oxide, among these metallic oxides. The hydrophilization function of a photocatalyst enables it to raise a hydrophilic property further under existence of the ultraviolet rays acquired from indoor lighting, the incident light from an aperture, etc. Furthermore, effectiveness, such as antifouling and deodorization, is also expectable with the disassembler of a photocatalyst. It is desirable to form by the sol applying method using the sol of these oxides. The thing of a sol of various particle diameter and description is available, and the optimal thing can be chosen in order to make the crevice formed in the front face enter. Although the various metallic oxides of the above-mentioned [an oxide sol] are mentioned, a thing 50nm or less has desirable particle diameter especially. It is because it enters into the irregularity formed beforehand, so the surface area on the front face of a base material becomes large and a hydrophilic property increases further. Moreover, the approach of forming the coat of said oxide by the spatter or CVD is also desirable. According to a spatter or CVD, it becomes possible to form the coat which employed the irregularity of the hydrophilic composite before carrying out coat formation efficiently. By making processing temperature high in CVD or a spatter, it is possible to raise more endurance, such as alkali resistance and warm water-proof nature.
[0042] Moreover, it is also possible to fix metal particles to the outermost surface of a base material by the photoreduction method. In this case, a hydrophilic function can be raised by adding the metal which has the electron capture effectiveness. The metal which has the electron capture effectiveness means the metal which ionization tendencies, such as Pt, Pd, Au, Ag, Cu, nickel, Fe, Co, and Zn, are small, and self is easy to be returned. Two or more these metals may be used together. As for the mean particle diameter of these metals, it is desirable that it is 200nm or less. It is for preventing interference of

light, coloring by scattered reflection, and nebula.
[0043] Moreover, it is possible to also make the gap of the metal oxide layer particle formed in the base material front face fill up with the particle of a particle size smaller than the gap. By filling up a gap with a particle, surface area on the front face of a base material can be enlarged, and it leads to improvement in a hydrophilic property. Moreover, by the particle with which the gap was filled up, a metal oxide layer particle can be combined and the adhesion to a base material improves. As a particle of a particle size smaller than said gap, Sn, Ti, Ag, Cu, Zn, Fe, Pt, Co, Pd, nickel, etc. are mentioned. If filled up with the metal which has said electron capture effectiveness, improvement in the further hydrophilic property is expectable.
[0044] It is also possible to support the matter which has antibacterial in the outermost surface of composite. The matter or the matter of an inorganic system of an organic system is sufficient as the matter which has antibacterial here. When endurance, such as abrasion resistance, warm water-proof, and chemical resistance, is taken into consideration, use of metals, such as Pt, Au, Ag, and Cu, or those compounds is desirable. Since the bacillus and microorganism which are one factor which checks a hydrophilic property by supporting the matter which has antibacterial [these] can be annihilated or propagation can be controlled, it is very effective when maintaining a hydrophilic property.
[0045]
[Example] Example 1:chain-like colloidal silica 1% -- chain-like colloidal silica (15 - 16% of solid content concentration, pH 2-4, particle diameter of 40-100nm) was diluted with ethanol, and 1% of the weight of coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.
[0046] Example 2:chain-like colloidal silica 20% -- included chain-like colloidal silica (15 - 16% of solid content concentration, pH 2-4, particle diameter of 40-100nm) in cloth, the mirror of 10cm angle was made to apply and season naturally it with an undiluted solution, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. Moreover, the angle of sweepback had initial drip nature at 15 degrees. The result is shown in Table 1.
[0047] Example 3:spherical colloidal silica 1% -- spherical -- to colloidal silica (solid content concentration [of 30 - 31%], particle diameter of 8-11nm);5g, surfactant;0.2g was added, it diluted with water, and 1% of the weight of coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.
[0048] Example 4:spherical colloidal silica 1% -- spherical colloidal silica (solid content concentration of 30 - 31%, particle diameter of 8-11nm) was diluted with water, and 1% of the weight of coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.
[0049] Example 5:alumina sol 1% -- cylindrical alumina sol (solid content concentration

of 20 - 22%, particle diameter of 10-20nm) was diluted with ethanol, and 1% of the weight of coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0050] Example 6:zirconia sol 1% -- the spherical zirconia sol (solid content concentration of 30 - 31%, particle diameter of 60-70nm) was diluted with ethanol, and 1% of the weight of coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0051] Example 7: With water, the titania sol 1% anatase mold titania sol (10% of solid content concentration) was diluted 10 times, and coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0052] Example 8: Included lithium silicate lithium silicate (20 - 21% of SiO2 solid-content concentration, 2 - 3.5% of Li2O solid content concentration) in cloth, the mirror of 10cm angle was made to apply and season naturally it with an undiluted solution, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0053] Example 9: Binder addition spherical colloidal silica (solid content concentration of 30 - 31%, particle diameter of 8-11nm); 10g, polyvinyl alcohol 5% water-solution (product [made from Japanese Synthetic chemistry], NH26);2g, silane coupling agent (Nippon Unicar make, A1100);0.02g, surfactant;0.4g, and water;90g were mixed, and coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0054] The example 1 of a comparison: For the comparison with the mirror aforementioned example, the mirror of 10cm angle which has not performed processing of what, either was prepared, and evaluation of the following five items was performed. Moreover, the angle of sweepback did not have initial drip nature at 22 degrees. The result is shown in Table 1.

[0055] evaluation-criteria 1. surface roughness (Ra) and irregularity -- the AFM (atomic force microscope) mode of average height (H) and a concavo-convex average (width-of-face L):scanning probe microscope (digital INSU vine face company make D3000) -- measurement.

2. Fog resistance : it contained for 5 minutes in the refrigerator (about 0 degree C), and was left under 28 degrees C and the ambient atmosphere of 81% of humidity after that, and surface cloudiness was checked.

O : -- it does not bloom cloudy at all but is uninfluential also in a reflected image -- **: to which a reflected image fades slightly although there is no O:cloudiness -- x: with the part which blooms cloudy slightly -- four steps of ** which blooms cloudy clearly -- evaluation.

3. Drip nature : install a sample in a perpendicular field, pour water, and check the ****** situation of 1 minute after visually.
O 100% of :water wetted areas, less than 100% of 80% or more of O:water wetted areas, less than [more than **:******** 60%80%], x : evaluate in four steps of less than 60% [of water wetted areas] **.
4. Abrasion resistance : perform sliding by sponge and check the abnormality existence of an appearance.
O : -- **: which completely has abnormality nothing and few [extent which turns out to hit O:light] blemishes -- four steps of ** with the deep blemish which reaches even x:base material with a shallow blemish -- evaluation.
5. Cleaning nature : pour water with an atomizer and check the ease of falling of dirt, after applying artificial dirt to a sample.
O x in which dirt remains but only with the water of three - four **:atomizers to which dirt falls completely with the water of :atomizer 1 time, and to which dirt falls completely with the water of three - four O:atomizers : even if it pours water, evaluate in four steps of ** where it hardly falls but dirt remains.
[0056]
[Table 1]

		Ra (nm)	H (nm)	L (nm)	防曇性	液滴性	耐摩耗性	清掃性
実施例1	鎖状コロイダルシリカ（1%）	3.37	10.09	51.02	◎	◎	◎	○
実施例2	鎖状コロイダルシリカ（20%＝原液）	2.46	7.67	51.42	◎	◎	◎	○
実施例3	球状コロイダルシリカ（1%、界面活性剤入）	1.56	4.80	32.04	◎	◎	○	◎
実施例4	球状コロイダルシリカ（1%、界面活性剤な	1.39	6.02	43.29	◎	◎	○	○
実施例5	棒状アルミナゾル（1%）	4.46	13.94	36.95	◎	◎	△	○
実施例6	ジルコニアゾル（1%）	0.18	0.85	9.26	○	◎	△	○
実施例7	チタニアゾル（1%）	0.57	2.46	11.34	○	◎	△	○
実施例8	リチウムシリケート（原液）	0.90	4.58	18.46	◎	◎	○	○
実施例9	球状コロイダルシリカ（1%、バインダー入）	2.12	5.78	46.82	◎	◎	◎	○
比較例1	処理なし	0.05	凹凸なし		×	×	◎	×

[0057] As shown in Table 1, it has checked that good fog resistance, drip nature, and cleaning nature were shown by applying various sols to a base material front face. Moreover, about particle shape, the spherical twist has also checked that the direction of a chain-like sol was excellent in abrasion resistance. Furthermore, when a spherical sol was used, it has checked that abrasion resistance improved by adding a binder.
[0058] Example 10: The coating liquid of the various concentration of 20% (with no dilution) - 0.01% of silica solid content concentration was adjusted for the evaluation chain-like colloidal silica (solid content concentration of 20%, particle diameter of 40-100nm) in various solid content concentration. the coating liquid of these various concentration -- 10 g/m2 -- it was made to contain in each sponge, and applied to the transparence glass plate, and the sample was obtained. Transparency, fog resistance, and

drip nature were evaluated about the various samples created by the above. About fog resistance and drip nature, it evaluated like the example of examples 1-9. transparency -- O: -- however it might carry out, the interference fringe was evaluated in four steps of ** which has [to which O:light which is not visible is hit] x; interference fringe and nebula with **:interference fringe whose interference fringe can be seen in whether it melts. Moreover, the workability for applying was also evaluated so that said three items might be satisfied. The evaluation result is shown in Table 2.

[0059]

[Table 2]

固形分濃度	透明性	防曇性	流滴性	塗布作業性
20%	○	◎	◎	透明な膜形成には、やや技術を要す
10%	◎	◎	◎	問題なし
1%	◎	◎	◎	問題なし
0.1%	◎	◎	◎	問題なし
0.05%	◎	○	◎	被だれが生じやすく、やや技術を要す
0.01%	○	×	△	被だれが生じ、非常に困難

[0060] As shown in Table 2, in the case of the sol applying method, it has checked that the solid content concentration for satisfying both transparency fog resistance and drip nature was 20% - 0.05%.

[0061] Example 11: The silica was coated on the polyethylene terephthalate (PET) film by antifog and the antifouling evaluation DC reactivity spatter of various films. This film was stuck on the mirror and the sample 1 was obtained. The silica was similarly coated on the PET film by EB vacuum evaporationo. This film was stuck on the mirror and the sample 2 was obtained. Moreover, the PET film top alumina was similarly coated by EB vacuum evaporationo. This film was stuck on the mirror and the sample 3 was obtained. For the comparison, also about the PET film which is the base material of samples 1-3, it stuck on the mirror and the comparison sample was obtained.

[0062] The following evaluation was performed to these samples.

1. Surface roughness (Ra), concavo-convex average height (H), and concavo-convex average width of face (L) : measure in the AFM (atomic force microscope) mode of a scanning probe microscope (digital INSU vine face company make D3000).

2. Fog resistance : contain for 5 minutes in a refrigerator (about 0 degree C), leave it under 28 degrees C and the ambient atmosphere of 81% of humidity after that, and check surface cloudiness. Initial fog resistance and the fog resistance after one-week exposure are evaluated.

O : -- it does not bloom cloudy at all but is uninfluential also in a reflected image -- **: to which a reflected image fades slightly although there is no O:cloudiness -- x: with the part which blooms cloudy slightly -- four steps of ** which blooms cloudy clearly -- evaluation.

3. Antifouling property : check the dirt adhesion situation after one-week exposure visually.

O : adhesion of dirt is not accepted but maintains an early detergency. O : although dirt has adhered slightly, evaluate in four steps of ** with the part which is uninfluential in use and **:dirt has adhered and a mirror cannot appear easily in which the front face bloomed cloudy with x:dirt.

In addition, exposure of a sample was installed in the mirror lower part in the shower booth of 80cm around for one week, and was performed by repeating bathing of four

persons per day. The evaluation result is shown in Table 3.
[0063]
[Table 3]

		Ra (nm)	H (nm)	L (nm)	初期防曇性	暴露後防曇性	暴露後防汚性	耐摩耗性
実施例11	DC反応性スパッタ（シリカ）	0.99	3.12	21.98	◎	◎	◎	−
	EB蒸着（シリカ）	0.83	2.40	18.32	◎	◎	◎	−
	EB蒸着（アルミナ）	0.86	3.99	17.91	◎	◎	◎	−
	比較例 PETフィルム	1.31	凹凸なし		×	×	×	−
実施例12	ケミカルエッチング（フッ酸処理）	0.47	1.92	20.94	◎	◎	◎	−
実施例13	ケミカルエッチング（ケイフッ化水素酸処	4.63	20.82	44.43	◎	◎	◎	−
実施例14	CVD法（酸化スズ）	9.26	33.92	59.36	◎	◎	◎	−
	耐温水試験	異常無し			−	◎	◎	−
	耐アルカリ試験	異常無し			−	◎	◎	−
実施例15	ケミカルエッチング＋シリカゾル	3.06	11.63	24.51	◎	◎	◎	−
実施例16	ケミカルエッチング＋チタニアゾル	4.02	18.11	38.11	◎	◎	◎	−
実施例17	ケミカルエッチング＋チタンアルコキシド	3.25	9.79	64.49	◎	◎	◎	◎
実施例18	真空蒸着（シリカ）＋スパッタ（チタニア）	3.02	12.78	29.99	◎	◎	◎	−
実施例19	スパッタ（チタニア）	8.51	38.19	57.62	−	−	−	−
	スパッタ（チタニア）＋スパッタ（酸化スズ）	2.39	10.43	25.66	◎	◎	◎	−

[0064] As shown in Table 3, fog resistance did not have the comparison sample. On the other hand, all of samples 1-3 showed the good fog resistance after [not both] one-week exposure have [fog resistance] effect in a reflected image the first stage. Moreover, about antifouling property, dirt adheres and, as for the comparison sample, the front face bloomed cloudy. On the other hand, neither of samples 1-3 was accepted, but adhesion of dirt was maintaining the early detergency for it. It has checked that good fog resistance and antifouling property were acquired by covering the inorganic oxide of a silica and an alumina with DC reactivity spatter and EB vacuum evaporationo to a base material, and forming irregularity.
[0065] Example 12: Hydrofluoric acid treatment (chemical etching)
The mirror front face of 20cm angle was chemically etched by fluoric acid, detailed irregularity was formed, and the sample was obtained. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.
[0066] As shown in Table 3, the good fog resistance after [not both] one-week exposure have [fog resistance] effect in a reflected image was shown the first stage. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that good fog resistance and antifouling property were acquired from this by forming irregularity in a front face by hydrofluoric acid treatment.

[0067] Example 13: Processing by the silicofluoric-acid solution (chemical etching)
By processing the mirror of 20cm angle with a silicofluoric-acid solution, detailed irregularity was formed and the sample was obtained. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.
[0068] As shown in Table 3, the good fog resistance after [not both] one-week exposure have [fog resistance] effect in a reflected image was shown the first stage. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that good fog resistance and antifouling property were acquired from this by forming irregularity in a front face by processing by the silicofluoric-acid solution.
[0069] Example 14: CVD method (tin oxide)
With the CVD method, the mirror front face of 20cm angle was coated with the tin oxide, and the sample was obtained. This sample was equally divided into three and the same evaluation as an example 11 was performed using one sheet. Warm water-proof nature and alkali resistance were evaluated using the two remaining sheets. Evaluation of warm water-proof nature was the approach of checking the existence of the abnormalities of an appearance visually after being immersed in 95-degree C warm water for 12 hours, and after alkali-proof evaluation was immersed in NaOH 5% for 12 hours, it was performed by the approach of checking the existence of the abnormalities of an appearance visually. The same evaluation as an example 11 was performed using the sample which evaluated warm water-proof nature and alkali resistance. The evaluation result is shown in Table 3.
[0070] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that the abnormalities by warm water and alkali were not accepted, but there was no effect also in fog resistance and antifouling property. It has checked that fog resistance and antifouling property strong also against warm water and alkali were acquired by carrying out the coat of the tin oxide with a CVD method, and forming irregularity from this.
[0071] Example 15: By processing with the processing silicofluoric-acid solution by the inorganic oxide sol of a concavo-convex front face, the mirror front face in which detailed irregularity was formed was coated with three kinds of sols for what mixed spherical colloidal silica (solid content concentration [of 30 - 31%], particle diameter of 8-11nm), and lithium silicate, and said spherical colloidal silica and said lithium silicate, respectively, and three kinds of samples were obtained. When irregularity was formed in the mirror front face, nebula was accepted slightly, but by coating said three kinds of sols, even if the front face hit light, an interference fringe and nebula were not accepted at all. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.
[0072] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that good fog resistance and antifouling property were acquired by carrying out coat formation with a metallic oxide further, and making irregularity from this, the base material front face which formed irregularity beforehand.
[0073] Example 16: The processing anatase mold titania sol (15% of solid content concentration) by the titanium oxide sol of a concavo-convex front face was diluted with

ethanol 15 times, and coating liquid was adjusted. Apply the above-mentioned coating liquid to the mirror front face which formed detailed irregularity by silicofluoric-acid solution processing by the flow coating method, it was made to season naturally, and the sample was obtained. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.

[0074] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that good fog resistance and antifouling property were acquired by applying a metallic-oxide sol to the base material front face which formed irregularity beforehand further, and forming irregularity in it from this.

[0075] Example 17: The processing titanium alkoxide solution (the Nippon Soda make, NDH510C, 5% of solid content concentration) by the alkoxide of a concavo-convex front face was diluted with ethanol twice, and coating liquid was adjusted. It applied to the mirror front face which formed detailed irregularity for the above-mentioned coating liquid by silicofluoric-acid solution processing by the flow coating method, it calcinated at 500 degrees C for 30 minutes, and the sample was obtained. The same evaluation and wear-resistant evaluation as an example 11 were performed using this sample. Wear-resistant evaluation was performed by the same approach as examples 1-9. The evaluation result is shown in Table 3.

[0076] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. In antifriction evaluation, a blemish did not stick at all. It has checked that wear-resistant good irregularity could be formed in the base material front face which formed irregularity beforehand from this by carrying out coat baking of the metallic oxide further. Moreover, it has also checked that good fog resistance and antifouling property were acquired.

[0077] Example 18: The silica was coated with the spatter processing vacuum evaporation technique of a concavo-convex front face, the mirror front face of 20cm angle which formed irregularity beforehand was further coated with the titania by the spatter, and the sample was obtained. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.

[0078] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that still better fog resistance and antifouling property were acquired from this by giving irregularity to the base material front face which carried out concavo-convex formation with vacuum deposition further.

[0079] Example 19: The titania was coated by spatter processing 2 spatter of a concavo-convex front face, the mirror front face of 20cm angle in which predetermined irregularity was formed was further coated with the tin oxide by the spatter, and the sample was obtained. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.

[0080] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown.

Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that still better fog resistance and antifouling property were acquired from this by giving irregularity to the base material front face which carried out concavo-convex formation by the spatter further.

[0081] Example 20: By the related spatter of thickness, and antifog and antifouling property, the mirror front face of 20cm angle was coated with the titania by various thickness, and the sample was obtained. The approach estimated antifog and antifouling property like the example 11 using this sample. It united and appearance evaluation was also performed. The approach is the same as that of examples 1-9. An evaluation result is shown in Table 4.

[0082]

[Table 4]

膜厚	Ra (nm)	H (nm)	L (nm)	外観	初期防曇性	暴露後防曇性	暴露後防汚性
300nm	6.65	27.56	43.79	◎	◎	◎	◎
400nm	7.16	29.14	46.01	◎	◎	◎	◎
500nm	8.51	38.19	57.62	△	◎	◎	◎

[0083] Although there was no difference in antifog and antifouling property by the difference in thickness within the limits of this experiment as shown in Table 4, by 500nm, the interference fringe was seen for thickness, and the exterior had a problem. From this, thickness has checked that 400nm or less was desirable.

[0084] The mirror front face was coated with five kinds of metallic-oxide sols, example 21 alumina sol, a silica sol, a tin-oxide sol, a titania sol, and a zirconia sol, respectively, and the sample was obtained. After measuring surface roughness (Ra), concavo-convex average height (H), the concavo-convex average width of face (L), and the zero charge point of each sample, it installed in the bath interior of a room, and was exposed for two weeks. Bathing made throughout [exposure term] four persons per day, and we decided to perform the intentional water or intentional ** to a mirror plane, no washing, etc. It was exposed by installing a normal mirror similarly for a comparison. In addition, a zero charge point is pH of a water solution in case F-potential is set to 0, and when it puts in into the water solution of pH higher than the value of a zero charge point, when F-potential puts in into the water solution of pH lower than it, it just becomes negative. The zero charge point measurement on the front face of a mirror calculated pH of an electrolyte water solution when an electroendosmose style is measured as a monitor particle of light scattering and an electroendosmose style is set to 0 in polystyrene latex with the titrimetric method using the laser F-potential meter (the product made from the Otsuka electron, ELS-6000). Surface roughness (Ra), concavo-convex average height (H), and concavo-convex average width of face (L) were measured in the AFM (atomic force microscope) mode of a scanning probe microscope (digital INSU vine face company make D3000). The sample was taken out from the bathroom after two-week exposure, and four-step evaluation by viewing was carried out according to the drip nature evaluation approach of examples 1-9. The result is shown in the following table.

[0085]

[Table 5]

試料	Ra (nm)	H (nm)	L (nm)	零電荷点	流滴性評価
アルミナ	4.46	13.94	36.95	7.5	△
シリカ	3.37	10.09	51.02	3.6	◎
酸化スズ	2.79	9.84	24.57	5.4	○
チタニア	0.57	2.46	11.34	6.0	○
ジルコニア	0.18	0.85	9.26	5.5	○
ノーマル鏡	0.05	凹凸なし		3.6	×

[0086] Although the Normal mirror had the zero charge point equivalent to the silica sol mirror as shown in Table 5, the water wetted area was not filled to 60%. On the other hand, in the mirror which applied various sols, the silica mirror showed [the alumina mirror / the tin-oxide zirconia mirror] 100% of water wetted area 80% or more 60% or more. As mentioned above, it has checked that it was hard to maintain a hydrophilic property only with detailed irregularity as the value of a zero charge point was small (F-potential is negative). that is, detailed irregularity and a zero charge point are less than seven (it sets to underwater [of the pH7 neighborhood] and F-potential is negative) -- union ****** -- it has checked that could maintain a good hydrophilic property and fog resistance, antifouling property, waterdrop formation tightness, and waterdrop adhesion tightness were acquired by water screen formation, so that a zero charge point is still lower by things.

[0087] It was immersed in 80-degree C warm water for 24 hours, nature was made to dry example 22 mirror after that, and the sample was obtained. This sample was evaluated like the example 19. Consequently, surface roughness (Ra) was [3.094nm and the concavo-convex average width of face (L) of 0.675nm and concavo-convex average height (H)] 24.899nm. All are O and evaluation of initial fog resistance, after [exposure] fog resistance, and antifouling property has checked that fog resistance and a detergency even with after [good] exposure could be maintained. It has checked that fog resistance and antifouling property also with good also forming irregularity in a base material front face by warm water immersion were acquired from this.

[0088] The example 23200mmx300mm mirror was prepared. The sample which applied the silica sol and formed irregularity was obtained. The silver-nitrate water solution was applied on it after concavo-convex formation by the silica sol, and the sample which carried out photoreduction immobilization of the silver using the BLB lamp was obtained. The sample which fixed direct silver to the mirror front face was also prepared for the comparison. The spore of mold was made to adhere to a front face after measurement, the surface roughness (Ra) of these samples, concavo-convex average height (H), and concavo-convex average width of face (L) were installed in the bath interior of a room, and exposure was performed for two weeks. Bathing of an exposure term throughout took day for four persons per. After two weeks, while checking the generating situation of the dirt adhesion and mold, the same approach as examples 1-9 estimated drip nature. A result is shown in Table 6. In addition, surface roughness (Ra), concavo-convex average height (H), and concavo-convex average width of face (L) were measured in the AFM (atomic force microscope) mode of a scanning probe microscope (digital INSU vine face company make D3000).

[0089]
[Table 6]

	Ra (nm)	H (nm)	L (nm)	流滴性	カビ発生	汚れ付着
凹凸	2.65	7.97	50.31	△	あり	ほとんどなし
凹凸+銀	2.87	8.12	48.19	○	なし	ほとんどなし
銀	0.32	凹凸なし		×	なし	あり

[0090] As shown in Table 6, although the comparison sample did not generate mold on a front face, dirt had adhered and the antifog effectiveness by less than 60% of water wetted areas and the drip was in a situation which is not acquired. Dirt hardly adhered but the sample which formed irregularity by the silica held drip nature barely with 60% or more of water wetted areas. However, when mold occurred in spots in the front face, the part had lost the hydrophilic property and it was used, it was in the condition which is not desirable. On the other hand, in spite of having been as practically equal as the sample of the point in which, as for what fixed silver on the irregularity of a silica, surface roughness, and concavo-convex average height and width of face formed irregularity by the silica, mold did not adhere, either but, as for the water wetted area, maintained 80% or more and good drip nature. It has checked that generating of the mold on the front face of a member could be prevented, and a hydrophilic property could be maintained good by it by fixing silver on irregularity from this. As mentioned above, it was suggested by combining irregularity and an antibacterial metal that a hydrophilic property can maintain in the condition good for a long period of time.
[0091]
[Effect of the Invention] According to this invention, the amount of contamination addition of dirt became it is large and possible [offering the hydrophilic antifog mirror for bathrooms which was mainly excellent in the fog resistance which can be suitably used in a bathroom, a shower room, etc., dripproofness, antifouling property, and self-consecration nature under the environment which a lot of / continuously / steams and water require].

TECHNICAL FIELD

[Field of the Invention] The amount of contamination addition of this invention of dirt is large, and it relates mainly to the hydrophilic antifog mirror for bathrooms which was excellent in the fog resistance which can be suitably used in a bathroom, a shower room,

etc., dripproofness, antifouling property, and self-consecration nature under the environment which a lot of [continuously] steams and water require.

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PRIOR ART

[Description of the Prior Art] As an approach of preventing the cloudiness and dirt of a bathroom mirror, giving a hydrophilic property to a mirror front face is performed conventionally. The approach of applying hydrophilic matter which applies a surfactant to a mirror front face, such as an approach and a hydrophilic monomer polymer, as an approach of giving a hydrophilic property etc. is learned. By water-screen-izing the waterdrop which adhered to the front face with the surfactant, by absorbing water the moisture adhering to a mirror front face, adhesion and formation of waterdrop are prevented and, according to the approach of applying a hydrophilic monomer polymer etc., it becomes possible to prevent the cloudiness and dirt on the front face of a member according to the approach of applying a surfactant. Moreover, once it pours water on the mirror front face produced using the obscured glass which put the countless crack into the longitudinal direction and formed irregularity parallel to a front face in JP,7-236553,A, when a front face turns into a flat surface with the water which entered the crevice, it becomes transparent and blooming cloudy by the water screen and preventing is indicated.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, the amount of contamination addition of dirt became it is large and possible [offering the hydrophilic antifog mirror for bathrooms which was mainly excellent in the fog resistance which can be suitably used in a bathroom, a shower room, etc., dripproofness, antifouling property, and self-consecration nature under the environment which a lot of / continuously / steams and water require].

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] A surfactant and the hydrophilic matter tend to flow and fall off with moisture, and a problem has water in the durability of effect in this environment frequently like especially a bathroom. Moreover, if a hydrophilic monomer polymer absorbs water, a front face will become easy to get damaged softly. In using in the environment where the vapor pressure under an operating environment is high, like a bathroom especially, a coefficient of water absorption increases and the inclination becomes very remarkable. Furthermore, both the surfactant and the hydrophilic monomer polymer had the fault of being easy to adsorb the dirt in air etc. As for a bathroom, the cleaning agent used at the time of a shampoo and body washing besides being dirt, soap, **, sebum resulting from the metal ion in tap water, etc. especially the silicon oil which is also a moisturizing component in a rinse, the cation system surfactant for obtaining admiration smoothly, etc. especially have very many contaminations from which a mirror front face is changed to the property which becomes easy to crawl water by adhering to a mirror front face. Furthermore, they disperse directly at the time of a shampoo and body washing, disperse indirectly with a shower, or are in the situation of being easy to adhere. Moreover, in the bath interior of a room, by the part with especially irregularity, a microorganism tends to breed, a microorganism breeds on the mirror front face which gave irregularity, and a hydrophilic property may be prevented from moisture and the organic substance being abundance. thus, the environment where a variety of [a bathroom environment] dirt exists, and tends to adhere and where a contamination load is large -- it is -- in addition -- and since it is the environment which applies water frequently, it was that the above-mentioned mirror can demonstrate fog resistance and antifouling property, only while being able to hold the condition with an early pure mirror, and it cannot almost hold fog resistance and antifouling property for a long period of time
[0004] For a reason [more than / this invention], by the simple defecation approach of

extent on which water is poured with the shower which was the difficulty of implementation, a hydrophilic advanced front face is repeated, and it reappears, and aims at offering the hydrophilic antifog mirror for bathrooms which can maintain good antifog and antifouling property over a long period of time.

MEANS

[Means for Solving the Problem] It is made for 0.4nmor more 200nm or less and center line average surface roughness Ra to have the concavo-convex structure where the concavo-convex height and the width of face in the location of the arbitration on the front face of a base material which the layer which consists of a hydrophilic inorganic oxide is formed in the base material front face that this invention should solve the above-mentioned technical problem, and was measured with the atomic force microscope on said front face of a layer are 0.1nm or more 50nm or less formed. It may be concavo-convex average height of 40nm or less of 0.8nm or more, concavo-convex average width of face of 100nm or less of 9nm or more, and less than [more than center line average surface roughness Ra0.1nm10nm] more preferably. It is transparent by forming in a base material front face the layer which consists of a hydrophilic inorganic oxide, and forming such concavo-convex structure in a layer front face, and the following functions are demonstrated, without spoiling the texture of a base material.
(1) Since a hydrophilic side is fractal-structure (structure where a fractal dimension is 2.01-2.99 dimensions), it comes to present an advanced hydrophilic property. Therefore, an attached groundwater drop is water-screen-ized uniformly. Thereby, sufficient cloudy tightness is demonstrated also in the use in bathroom space with many steams.
(2) The water screen will be formed in a front face, if water is beforehand poured with the shower etc. just before use in order to present an advanced hydrophilic property. If this water screen exists, since a mirror front face excels a dirt component in the compatibility over water far, antifouling property will be demonstrated also in bathroom space with many dirt burdens. In bathroom space, since it is convenient even if a floor gets wet with water, it is available in this property, and only by pouring water with the shower etc. beforehand just before use each time at the long period of time, it continues at a long period of time, and prevention of not only fog resistance but the visibility fall by adhesion of soap etc. is attained in the time of use. Moreover, it is washed away by the shower which also mentioned above the dirt in the air which adhered at the time of un-using it.
(3) Since concavo-convex structure is very detailed, the bacillus or mold which are easy

to inhabit a bathroom cannot enter into irregularity. Therefore, the dirt by the bacillus or mold is also prevented.
(4) Since the hard layer which consists of an inorganic oxide is formed, a mirror front face cannot get damaged easily. Therefore, the fall of the visibility of the mirror by generating of a blemish can be prevented. It can ask for the height of the irregularity on the front face of a base material, width of face, and surface roughness using an atomic force microscope. Since the gas which entered the surface water of adsorption and a front face cannot interfere and an exact value cannot be known with the surface roughness plan of a contact process in case a complicated and detailed concavo-convex front face is measured, measuring using an atomic force microscope is desirable. As for concavo-convex height and width of face, it is desirable to carry out to 1/2 or less of the wavelength of the light, i.e., 200nm. It is because coloring of the surface layer by interference of light can be prevented and texture of a base material is not spoiled. Moreover, as for concavo-convex height and width of face, it is desirable that it is 0.4nm or more. It is because sufficient mechanical reinforcement is securable. Surface roughness is mainly decided by concavo-convex height, and is set to surface roughness (Ra) = height / 4 in the cross section of the typical front face shown in drawing 1. Since it is desirable here that concavo-convex height is 0.4nm or more 200nm or less, 0.1nm or more 50nm or less of surface roughness is desirable.
[0006] In this invention, the fog resistance mirror for bathrooms characterized by including a silicic-acid alkali-metal salt in the hydrophilic inorganic oxide layer of said concavo-convex structure is offered further that the above-mentioned technical problem should be solved. According to this, by controlling the property to begin to melt gradually, self-consecration of the mirror front face is carried out over a long period of time, fixing of dirt is prevented without applying time and effort, and a pure and hydrophilic advanced front face is repeated simple, it reappears, and good antifog and antifouling property are made maintainable over a long period of time.
[0007] In this invention, the hydrophilic composite further characterized by said concavo-convex structure being fractal structure that the above-mentioned technical problem should be solved is offered. Fractal structure is multistage concavo-convex structure which includes the concavo-convex structure of a small period in the concavo-convex structure and structure of a large period on the surface of a base material. By carrying out to fractal structure, i.e., the complicated structure which has still finer irregularity in irregularity, the water holding capacity on the front face of a base material is heightened, and it becomes possible to make a still more advanced hydrophilic property discover.
[0008] In the desirable mode of this invention, said base material is formed by chemical etching. According to chemical etching, a clear reflected image without a twin image is acquired.
[0009] In the desirable mode of this invention, said base material is formed by warm water immersion. in order not to use a drug solution etc. according to warm water immersion -- safe -- in addition -- and irregularity can be formed simple.
[0010] Said base material is equipped with the layer containing one or more sorts of a metallic oxide joined to a base material front face in the desirable mode of this invention. By making one or more sorts of metallic oxides contain, the irregularity of the request which presents an advanced hydrophilic property can be formed easily.
[0011] It is made for the thickness of said layer to be set to 400nm or less in the desirable

mode of this invention. By considering as said thickness, the transparent film without an optical interference which has the outstanding fog resistance, or nebula can be formed.
[0012] In the desirable mode of this invention, said layer is formed by the sol applying method. According to the sol applying method, with the magnitude of a base material, and a configuration, since the constraint on a facility is not received, a special facility cannot be required but coat formation can be carried out on a base material front face simple.
[0013] In the desirable mode of this invention, said layer is formed with vacuum deposition. According to vacuum deposition, it is not based on the class of base material, and the class of oxide to be used, but it is uniform and the transparent film which has the outstanding fog resistance can be formed.
[0014] In the desirable mode of this invention, said layer is formed by sputtering. According to sputtering, the uniform and firm film can be formed.
[0015] In the desirable mode of this invention, said layer is formed by CVD. According to CVD, the better film of endurance can be formed.
[0016] In the desirable mode of this invention, a metallic oxide is chosen from the group which consists of a silica, an alumina, a zirconia, a titania, tin oxide, and a zinc oxide. By using these oxides, the hydrophilic advanced front face excellent in a water resisting property and chemical resistance is obtained. It is desirable to use what has a zirconia, a titania, the tin oxide, and the photocatalyst activity of a zinc oxide among these metallic oxides. By doing so, a much more advanced hydrophilic property can be acquired by the ultraviolet rays from indoor lighting and an indoor aperture.
[0017] In the desirable mode of this invention, **** was further formed for the silicic-acid alkali-metal salt as the principal component on the front face which has concavo-convex structure, the concavo-convex average height and the average width of face in the location of the arbitration of the outermost surface measured with the atomic force microscope are 0.4nm or more 200nm or less, and center line average surface roughness Ra is equipped with 0.1nm or more layer it is [layer] 50nm or less. It may be concavo-convex average height of 40nm or less of 0.8nm or more, concavo-convex average width of face of 100nm or less of 9nm or more, and less than [more than center line average surface roughness Ra0.1nm10nm] more preferably. A still better hydrophilic front face is obtained by forming irregularity further on the front face which formed irregularity beforehand. Moreover, even if an interference fringe and nebula are accepted, said front face cancels them and has the effectiveness made into transparence. Although it is not limited, in addition, surface concavo-convex structure is desirable, if structure according to claim 1 to 18 is made.
[0018] In the desirable mode of this invention, a concave convex layer is formed by the sol applying method. It is because the sol of a metallic oxide can obtain the thing of various particle diameter and description, so a suitable thing can be chosen according to the irregularity of the base material formed beforehand.
[0019] As for a concave convex layer, in the desirable mode of this invention, forming by sputtering is desirable. According to sputtering, the uniform and firm film can be formed.
[0020] In the desirable mode of this invention, a concave convex layer is formed by CVD. According to CVD, the better film of endurance can be formed.
[0021] As for the metallic oxide which forms a concave convex layer, in the desirable mode of this invention, it is desirable to choose out of the group which consists of a

silica, an alumina, a zirconia, a titania, tin oxide, and a zinc oxide. It is easy to obtain the good irregularity of a hydrophilic property by using these metallic oxides. It is desirable to use what has a zirconia, a titania, the tin oxide, and the photocatalyst activity of a zinc oxide among these metallic oxides. By doing so, a much more advanced hydrophilic property can be acquired by the ultraviolet rays from indoor lighting and an indoor aperture.

[0022] The 2-dimensional cross-section structure of a concavo-convex hole has the largest surface section, and it is made to be so narrow that it go to the back in the desirable mode of this invention. The surface section has the largest 2-dimensional cross-section structure of a hole, and if a configuration which is so narrow that it goes to the back is carried out, even if stained with dirt, it will be easy to fall, and it will become possible to maintain a good hydrophilic property.

[0023] It is made for an angle of sweepback with water [in / in said mirror / an elevation surface] to have the hydrophilic property of 20 or less degrees in the desirable mode of this invention. It is because the water which adhered to the mirror front face in the elevation surface shows drip nature and becomes easy to present antifouling property, fog resistance, waterdrop formation tightness, and waterdrop adhesion tightness over the whole mirror surface. Drip nature does not serve as waterdrop, when water is poured, but it means the condition of having formed the water screen in the mirror plane in elevation surfaces, such as a wall of a bathroom. Moreover, an angle of sweepback is a contact angle of the water when dipping and pulling up a sample in a tank with constant speed.

[0024] The matter which has antibacterial is supported by the outermost surface of composite in the desirable mode of this invention. Since the bacillus and microorganism which are one factor which checks a hydrophilic property by supporting the matter which has antibacterial can be annihilated or propagation can be controlled, a good hydrophilic property becomes maintainable.

[0025] In the desirable mode of this invention, underwater F-potential of pH7 near [a composite front face] is made negative. By making F-potential negative, when water contacts a mirror front face, disinfection and/or the antifouling effectiveness can be given. It is known that the dirt, the fungus, etc. of the circumference of water are generally charged in negative in underwater [of the pH7 neighborhood]. Therefore, by making negative F-potential on the front face of composite, where water is contacted, a composite front face, and dirt and a fungus can oppose electrically, and can prevent adhesion of dirt and a fungus.

[0026]

[Embodiment of the Invention] The fog resistance mirror of this invention can be suitably used mainly as a hydrophilic antifog mirror for bathrooms which was excellent in fog resistance, dripproofness, antifouling property, and self-consecration nature in the bathroom, the shower room, etc. under [of the circumference of water] the environment which the amount of contamination addition of dirt is especially large, and a lot of [continuously] steams and water require.

[0027] In this invention, as an approach of forming irregularity in a base material front face Although what is necessary is just to choose from the well-known approach instead of what is limited, the sol applying method, Like drawing 2 therefore by the approach of forming film which has detailed irregularity on a base material front face, such as the galvanizing method, a CVD method, sputtering, and a vacuum deposition method,

sandblasting, etching, etc. Like drawing 3 , there are an approach of forming direct irregularity in a base material, the approach of forming detailed irregularity on a die and imprinting irregularity to a base material, etc. After forming irregularity in a transparent base material front face, a reflective coat may be given and mirror-ized at the rear face, and irregularity may be formed after giving and mirror-izing a reflective coat at the rear face previously.

[0028] In this invention, silicic-acid sodium, a silicic-acid potassium, a silicic-acid lithium, and silicic-acid AMMOUMU can use suitably as a silicic-acid alkali-metal salt.

[0029] In this invention, it is desirable to form irregularity in a base material front face by chemical etching. Chemical etching is the approach make the steam which generates a base material when immersion or its solution is warmed in the solution of an acid, alkali, and a peroxide contact, and the chemical reaction performs surface treatment. As a solution to be used, water solutions, such as a hydrochloric acid, a sulfuric acid, an ammonium sulfide, fluoric acid, boron fluoride, and a silicofluoric acid, are mentioned.

[0030] In this invention, it is desirable to form irregularity in a base material front face by warm water immersion. in order not to use a drug solution etc. according to warm water immersion -- safe -- in addition -- and irregularity can be formed simple. Water may also be pure water or tap water anything. When the processing time is taken into consideration, 60 degrees C or more of water temperature are [that what is necessary is just 40 degrees C or more] desirable.

[0031] In this invention, it is desirable to carry out covering formation of the layer containing one or more sorts of a metallic oxide on a base material front face. According to this, the irregularity of the request which presents an advanced hydrophilic property can be formed easily. as the approach of carrying out covering formation of said oxide -- from well-known approaches, such as the sol applying method, vacuum deposition, sputtering, a CVD method, and the galvanizing method, -- you may choose -- moreover -- other than this . According to the sol applying method, with the magnitude of a base material, and a configuration, since the constraint on a facility is not received, a special facility cannot be required but it can carry out simple. According to a CVD method, sputtering, and vacuum deposition, although the application to a big base material receives constraint on a facility, it becomes possible [forming the uniform and stabilized thin film]. By making processing temperature high in these approaches, it is possible to raise more endurance, such as alkali resistance and warm water-proof nature.

[0032] It is made for the thickness of the coat of said oxide to be set to 400nm or less in this invention. When the coat which exceeds 400nm especially with one kind of oxide is formed, the interference fringe by interference of light, nebula, etc. occur, and it is easy to produce exterior fault. Moreover, if thickness becomes thick, abrasion resistance will fall, and becoming easy to attach a blemish is not avoided, either.

[0033] As a metallic oxide here A silica, an alumina, a zirconia, Seria, Yttria, BORONIA, a magnesia, calcia, a ferrite, hafnia, Titanium oxide, a zinc oxide, a tungstic trioxide, ferric oxide, a cuprous oxide, A cupric oxide, bismuth(III) oxide, the tin oxide, nickel oxide, cobalt oxide, Single oxides, such as barium oxide, a strontium oxide, and a vanadium oxide, Multiple oxides, such as barium titanate, a calcium silicate, water glass, an aluminosilicate, calcium phosphate, strontium titanate, potassium titanate, barium titanate, titanic-acid calcium, and aluminosilicate, can use suitably. Especially, it is desirable to use a silica, an alumina, a zirconia, a titania, the tin oxide, or a zinc oxide. A

silica and an alumina are good for forming small fine irregularity, and a zirconia, a titania, the tin oxide, and a zinc oxide are desirable for forming big irregularity. In the sol applying method, a silica with various available things is desirable about the description of particle diameter and the sol mentioned later. The silica is the cheapest and its practicality is very high. Moreover, an advanced hydrophilic property can be acquired by using the silica whose F-potential is negative, a zirconia, a titania, and the tin oxide in underwater [of the pH7 neighborhood]. It is using a desirable silica with the lowest surface potential, and a still more advanced hydrophilic property can be acquired by use of a silica.

[0034] As for a metallic-oxide particle, in this invention, it is desirable to consider as the gestalt of the sol which water or a hydrophilic solvent was made to distribute to colloid. Although it is not limited as long as make stability distribute said metallic oxide as a hydrophilic solvent, it makes homogeneity and a smooth coat form on a base material and it gets especially, as a desirable thing, the boiling point can mention an organic solvent 200 degrees C or less. As an example of a desirable organic solvent, a methanol, ethanol, n-propanol, Isopropanol, t-butanol, isobutanol, n-butanol, 2-methyl propanol, a pentanol, ethylene glycol, mono-acetone alcohol, Diacetone alcohol, ethylene glycol monomethyl ether, 4-hydroxy-4-methyl-2-pentanone, Dipropylene glycol, propylene glycol, tripropylene glycol, 1-ethoxy-2-propanol, 1-butoxy-2-propanol, 1-propoxy-2-propanol, propylene glycol monomethyl ether, Dipropylene glycol monomethyl ether, dipropylene glycol mono-ethyl ether, Ester solvents, such as hydrocarbon system solvents, such as alcohols solvents, such as tripropyllene glycol monomethyl ether and 2-butoxyethanol, and n-hexane, toluene, a xylene, a mineral spirit, methyl acetate, ethyl acetate, and butyl acetate, can be mentioned.

[0035] In this invention, when carrying out coat formation on a base material front face by the sol applying method, it is desirable to use the coating constituent made into a metallic oxide 0.05 - 20 weight sections, and a solvent 99.95 - 80 weight sections. By applying said coating liquid to a base material front face, it has the outstanding fog resistance and the transparent film without an optical interference or nebula can be formed.

[0036] Moreover, when based on the sol applying method, it is desirable to use the shape of feathers with a chain-like metallic oxide with a granular metallic oxide with a mean particle diameter of 1-100nm, a pitch diameter [of 1-50nm], and an average die length of 10-1000nm, a pitch diameter [of 1-50nm], and an average die length of 10-500nm or a cylindrical metallic oxide. As a granular metallic oxide with a mean particle diameter of 1-100nm, a silica, an alumina, etc. are mentioned as a chain-like metallic oxide with a pitch diameter [of 1-50nm], and an average die length of 10-1000nm, and a silica, a zirconia, etc. are mentioned for an alumina, a titania, etc. as the shape of feathers with a pitch diameter [of 1-50nm], and an average die length of 10-500nm, and a cylindrical metallic oxide. If the shape of the shape of a chain and feathers and a cylindrical metallic oxide are used, the endurance of the film formed in the base material front face can be raised. Moreover, if a granular inorganic oxide is used, after having desired irregularity, the film with more high smooth nature can be formed.

[0037] In this invention, it is desirable to make a base material surface layer contain the binder for fixing said metallic oxide to said base material front face. It is because the adhesion on the front face of a base material improves with a binder and still more

advanced endurance and abrasion resistance are obtained. As a binder, the binder of quality of organic, such as a binder of minerals, such as a cover coat, water glass, and silicone, thermosetting resin, a photo-setting resin, and thermoplastics, etc. can be used.
[0038] In this invention, a surfactant can be included in said coating liquid. As an example of the surface active agent which can be added, sulfonic-acid polyoxyethylene-alkyl-phenyl-ether ammonium salt, Sulfonic-acid polyoxyethylene-alkyl-phenyl-ether sodium salt, Fatty-acid potash soap, fatty-acid sodium soap, sodium dioctyl sulfosuccinate, Alkyl sulfate, alkyl ether sulfate, alkyl sulfate specific salt, Alkyl ether sulfate specific salt, polyoxyethylene-alkyl-ether sulfate, Polyoxyethylene-alkyl-ether sulfate specific salt, an alkyl sulfate TEA salt, A polyoxyethylene-alkyl-ether sulfate TEA salt, 2-ethylhexyl alkyl-sulfuric-acid ester sodium salt, Acyl methyl taurine acid sodium, lauroyl methyl taurine acid sodium, Sodium dodecylbenzenesulfonate, sulfo succinic-acid lauryl disodium, Polyoxyethylene sulfo succinic-acid lauryl disodium, polycarboxylic acid, TO me -- oil ZARUKOSHIN, AMIDOE-TERUSARUFE-TO, and lauroyl ZARUKOSHINE - Anionic surface active agents, such as sulfo FA ester sodium salt; Polyoxyethylene RAURIRUE-Tell, Polyoxyethylene TORIDESHIRUE-Tell, polyoxyethylene ASECHIRUE-Tell, Polyoxyethylene stearylether, polyoxyethylene OREIRUE-Tell, Polyoxyethylene alkyl ether, polyoxyethylene alkyl ester, The polyoxyethylene alkylphenol ether, polyoxyethylene nonyl phenyl ether, Polyoxyethylene octyl phenyl ether, polyoxyethylene RAURA-TO, Polyoxyethylene stearate, polyoxyethylene alkyl phenyl ether, Polyoxyethylene oleate, sorbitan alkyl ester, polyoxyethylene sorbitan alkyl ester, Polyether denaturation silicon, polyester denaturation silicon, sorbitan RAURA-TO, Sorbitan stearate, sorbitan palmitate, sorbitan sesquioleate, Sorbitan oleate, polyoxyethylene sorbitan RAURA-TO, Polyoxyethylene sorbitan stearate, polyoxyethylene sorbitan palmitate, Polyoxyethylene sorbitan oleate, glycero-RUSUTEARE-TO, Polyglyceryl fatty acid ester, alkyl ARUKIRO-RUAMIDO, lauric-acid diethanolamide, Oleic acid diethanolamide, an oxyethylene dodecyl amine, a polyoxyethylene dodecyl amine, Polyoxyethylene alkylamine, a polyoxyethylene octadecyl amine, Polyoxyethylene alkyl propylenediamine, polyoxyethylene oxypropylene block polymer, Nonionic surface active agents, such as polyoxyethylene stearate; A dimethyl alkyl betaine, Amphoteric surface active agents, such as an alkyl glycine, an amide betaine, and imidazoline; Octadecyl dimethylbenzyl ammoniumchloride, Alkyldimethyl benzyl ammoniumchloride, tetradecyl dimethylbenzyl ammoniumchloride, Dioleoyl dimethylannmonium chloride, the 4th class salt of 1-hydroxy-2-alkyl imidazoline, An alkyl iso quinolinium star's picture, a giant-molecule amine, octadecyl trimethylammonium chloride, Alkyl trimethylammonium chloride, dodecyl trimethylammonium chloride, Hexadecyl trimethylammonium chloride, behenyl trimethylammonium chloride, Cationic surfactants, such as the 4th class salt of alkyl imidazoline, dialkyl dimethylannmonium chloride, octadecyl amine acetate, tetradecylamine acetate, alkyl propylenediamine acetate, and JIDESHIRU dimethylannmonium chloride, etc. are mentioned.
[0039] In this invention, that what is necessary is just to choose suitably the approach of applying said coating liquid to a base material front face from a well-known approach, although the spray coating method using an air gun, an air loess gun, an aerosol spray, etc., a spin coating method, a DIP coating method, the flow coating method, the roll coating method, brush painting, sponge coating, etc. are raised, it is not limited to these.

Moreover, various shampoos, primers and a cleaning agent, compounds, an antistatic agent, etc. can also be used as processing before applying said coating liquid to a base material front face.

[0040] Which approach may be [that what is necessary is just to perform suitably heat treatment after applying coating liquid to a base material front face according to the class and property of coating liquid and a base material] used for air drying, heating, infrared radiation, UV irradiation, etc. A solvent may only be vaporized, it may dry and a request may also be good. Although a finishing agent is applied on the surface of goods and subsequently being heat-treated as an approach in the case of heat-treating, the count of spreading and heat treatment may be 2 times or more. After repeating only spreading two or more times, various approaches, such as heat-treating by once and performing a series of actuation of spreading and heat treatment two or more times, are mentioned.

[0041] In this invention, it is also possible to form the concave convex layer which consists of a metallic oxide further like drawing 4 on the base material front face which formed irregularity beforehand. Although what is necessary is just to choose from a well-known approach the irregularity formed beforehand, it is desirable to form by the sol applying method, the vacuum deposition method, sputtering, and CVD as mentioned above, and, as for the concavo-convex structure, it is desirable to go into the range of above-mentioned concavo-convex height, width of face, and surface roughness. As a metallic oxide which forms a concave convex layer, although what is necessary is just to choose from the above-mentioned metallic oxides, it is desirable to use a silica, an alumina, a zirconia, a titania, the tin oxide, and a zinc oxide especially. It is desirable to use what has photocatalyst activity, such as a zirconia, a titania, tin oxide, and a zinc oxide, among these metallic oxides. The hydrophilization function of a photocatalyst enables it to raise a hydrophilic property further under existence of the ultraviolet rays acquired from indoor lighting, the incident light from an aperture, etc. Furthermore, effectiveness, such as antifouling and deodorization, is also expectable with the disassembler of a photocatalyst. It is desirable to form by the sol applying method using the sol of these oxides. The thing of a sol of various particle diameter and description is available, and the optimal thing can be chosen in order to make the crevice formed in the front face enter. Although the various metallic oxides of the above-mentioned [an oxide sol] are mentioned, a thing 50nm or less has desirable particle diameter especially. It is because it enters into the irregularity formed beforehand, so the surface area on the front face of a base material becomes large and a hydrophilic property increases further. Moreover, the approach of forming the coat of said oxide by the spatter or CVD is also desirable. According to a spatter or CVD, it becomes possible to form the coat which employed the irregularity of the hydrophilic composite before carrying out coat formation efficiently. By making processing temperature high in CVD or a spatter, it is possible to raise more endurance, such as alkali resistance and warm water-proof nature.

[0042] Moreover, it is also possible to fix metal particles to the outermost surface of a base material by the photoreduction method. In this case, a hydrophilic function can be raised by adding the metal which has the electron capture effectiveness. The metal which has the electron capture effectiveness means the metal which ionization tendencies, such as Pt, Pd, Au, Ag, Cu, nickel, Fe, Co, and Zn, are small, and self is easy to be returned. Two or more these metals may be used together. As for the mean particle diameter of these metals, it is desirable that it is 200nm or less. It is for preventing interference of

light, coloring by scattered reflection, and nebula.
[0043] Moreover, it is possible to also make the gap of the metal oxide layer particle formed in the base material front face fill up with the particle of a particle size smaller than the gap. By filling up a gap with a particle, surface area on the front face of a base material can be enlarged, and it leads to improvement in a hydrophilic property. Moreover, by the particle with which the gap was filled up, a metal oxide layer particle can be combined and the adhesion to a base material improves. As a particle of a particle size smaller than said gap, Sn, Ti, Ag, Cu, Zn, Fe, Pt, Co, Pd, nickel, etc. are mentioned. If filled up with the metal which has said electron capture effectiveness, improvement in the further hydrophilic property is expectable.
[0044] It is also possible to support the matter which has antibacterial in the outermost surface of composite. The matter or the matter of an inorganic system of an organic system is sufficient as the matter which has antibacterial here. When endurance, such as abrasion resistance, warm water-proof, and chemical resistance, is taken into consideration, use of metals, such as Pt, Au, Ag, and Cu, or those compounds is desirable. Since the bacillus and microorganism which are one factor which checks a hydrophilic property by supporting the matter which has antibacterial [these] can be annihilated or propagation can be controlled, it is very effective when maintaining a hydrophilic property.

EXAMPLE

[Example] Example 1:chain-like colloidal silica 1% -- chain-like colloidal silica (15 - 16% of solid content concentration, pH 2-4, particle diameter of 40-100nm) was diluted with ethanol, and 1% of the weight of coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.
[0046] Example 2:chain-like colloidal silica 20% -- included chain-like colloidal silica (15 - 16% of solid content concentration, pH 2-4, particle diameter of 40-100nm) in cloth, the mirror of 10cm angle was made to apply and season naturally it with an undiluted solution, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. Moreover, the angle of sweepback had initial drip nature at 15 degrees. The result is shown in Table 1.
[0047] Example 3:spherical colloidal silica 1% -- spherical -- to colloidal silica (solid

content concentration [of 30 - 31%], particle diameter of 8-11nm);5g, surfactant;0.2g was added, it diluted with water, and 1% of the weight of coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0048] Example 4:spherical colloidal silica 1% -- spherical colloidal silica (solid content concentration of 30 - 31%, particle diameter of 8-11nm) was diluted with water, and 1% of the weight of coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0049] Example 5:alumina sol 1% -- cylindrical alumina sol (solid content concentration of 20 - 22%, particle diameter of 10-20nm) was diluted with ethanol, and 1% of the weight of coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0050] Example 6:zirconia sol 1% -- the spherical zirconia sol (solid content concentration of 30 - 31%, particle diameter of 60-70nm) was diluted with ethanol, and 1% of the weight of coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0051] Example 7: With water, the titania sol 1% anatase mold titania sol (10% of solid content concentration) was diluted 10 times, and coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0052] Example 8: Included lithium silicate lithium silicate (20 - 21% of SiO2 solid-content concentration, 2 - 3.5% of Li2O solid content concentration) in cloth, the mirror of 10cm angle was made to apply and season naturally it with an undiluted solution, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0053] Example 9: Binder addition spherical colloidal silica (solid content concentration of 30 - 31%, particle diameter of 8-11nm); 10g, polyvinyl alcohol 5% water-solution (product [made from Japanese Synthetic chemistry], NH26);2g, silane coupling agent (Nippon Unicar make, A1100);0.02g, surfactant;0.4g, and water;90g were mixed, and coating liquid was adjusted. Absorbed cloth with the above-mentioned coating liquid, the mirror of 10cm angle was made to apply and season naturally it, and the sample was obtained. Evaluation of the following five items was performed using the above-mentioned sample. The result is shown in Table 1.

[0054] The example 1 of a comparison: For the comparison with the mirror aforementioned example, the mirror of 10cm angle which has not performed processing of what, either was prepared, and evaluation of the following five items was performed.

Moreover, the angle of sweepback did not have initial drip nature at 22 degrees. The result is shown in Table 1.

[0055] evaluation-criteria 1. surface roughness (Ra) and irregularity -- the AFM (atomic force microscope) mode of average height (H) and a concavo-convex average (width-of-face L):scanning probe microscope (digital INSU vine face company make D3000) -- measurement.

2. Fog resistance : it contained for 5 minutes in the refrigerator (about 0 degree C), and was left under 28 degrees C and the ambient atmosphere of 81% of humidity after that, and surface cloudiness was checked.

O : -- it does not bloom cloudy at all but is uninfluential also in a reflected image -- **: to which a reflected image fades slightly although there is no O:cloudiness -- x: with the part which blooms cloudy slightly -- four steps of ** which blooms cloudy clearly -- evaluation.

3. Drip nature : install a sample in a perpendicular field, pour water, and check the ****** situation of 1 minute after visually.

O 100% of :water wetted areas, less than 100% of 80% or more of O:water wetted areas, less than [more than **:******** 60%80%], x : evaluate in four steps of less than 60% [of water wetted areas] **.

4. Abrasion resistance : perform sliding by sponge and check the abnormality existence of an appearance.

O : -- **: which completely has abnormality nothing and few [extent which turns out to hit O:light] blemishes -- four steps of ** with the deep blemish which reaches even x:base material with a shallow blemish -- evaluation.

5. Cleaning nature : pour water with an atomizer and check the ease of falling of dirt, after applying artificial dirt to a sample.

O x in which dirt remains but only with the water of three - four **:atomizers to which dirt falls completely with the water of :atomizer 1 time, and to which dirt falls completely with the water of three - four O:atomizers : even if it pours water, evaluate in four steps of ** where it hardly falls but dirt remains.

[0056]

[Table 1]

		Ra (nm)	H (nm)	L (nm)	防曇性	流滴性	耐摩耗性	清掃性
実施例1	鎖状コロイダルシリカ（1%）	3.37	10.09	51.02	◎	◎	◎	○
実施例2	鎖状コロイダルシリカ（20%=原液）	2.46	7.67	51.42	◎	◎	◎	○
実施例3	球状コロイダルシリカ（1%、界面活性剤入）	1.56	4.80	32.04	◎	◎	○	◎
実施例4	球状コロイダルシリカ（1%、界面活性剤な	1.39	6.02	43.29	◎	◎	○	○
実施例5	棒状アルミナゾル（1%）	4.46	13.94	36.95	◎	◎	△	○
実施例6	ジルコニアゾル（1%）	0.18	0.85	9.26	○	◎	△	○
実施例7	チタニアゾル（1%）	0.57	2.46	11.34	○	◎	△	○
実施例8	リチウムシリケート（原液）	0.90	4.58	18.46	◎	◎	○	○
実施例9	球状コロイダルシリカ（1%、バインダー入）	2.12	5.78	46.82	◎	◎	◎	○
比較例1	処理なし	0.05	凹凸なし		×	×	◎	×

[0057] As shown in Table 1, it has checked that good fog resistance, drip nature, and cleaning nature were shown by applying various sols to a base material front face. Moreover, about particle shape, the spherical twist has also checked that the direction of a chain-like sol was excellent in abrasion resistance. Furthermore, when a spherical sol was used, it has checked that abrasion resistance improved by adding a binder.

[0058] Example 10: The coating liquid of the various concentration of 20% (with no dilution) - 0.01% of silica solid content concentration was adjusted for the evaluation chain-like colloidal silica (solid content concentration of 20%, particle diameter of 40-100nm) in various solid content concentration. the coating liquid of these various concentration -- 10 g/m2 -- it was made to contain in each sponge, and applied to the transparence glass plate, and the sample was obtained. Transparency, fog resistance, and drip nature were evaluated about the various samples created by the above. About fog resistance and drip nature, it evaluated like the example of examples 1-9. transparency -- O: -- however it might carry out, the interference fringe was evaluated in four steps of ** which has [to which O:light which is not visible is hit] x; interference fringe and nebula with **:interference fringe whose interference fringe can be seen in whether it melts. Moreover, the workability for applying was also evaluated so that said three items might be satisfied. The evaluation result is shown in Table 2.

[0059]

[Table 2]

固形分濃度	透明性	防曇性	流滴性	塗布作業性
20%	○	◎	◎	透明な膜形成には、やや技術を要す
10%	◎	◎	◎	問題なし
1%	◎	◎	◎	問題なし
0.1%	◎	◎	◎	問題なし
0.05%	◎	○	◎	液だれが生じやすく、やや技術を要す
0.01%	○	×	△	液だれが生じ、非常に困難

[0060] As shown in Table 2, in the case of the sol applying method, it has checked that the solid content concentration for satisfying both transparency fog resistance and drip nature was 20% - 0.05%.

[0061] Example 11: The silica was coated on the polyethylene terephthalate (PET) film by antifog and the antifouling evaluation DC reactivity spatter of various films. This film was stuck on the mirror and the sample 1 was obtained. The silica was similarly coated on the PET film by EB vacuum evaporationo. This film was stuck on the mirror and the sample 2 was obtained. Moreover, the PET film top alumina was similarly coated by EB vacuum evaporationo. This film was stuck on the mirror and the sample 3 was obtained. For the comparison, also about the PET film which is the base material of samples 1-3, it stuck on the mirror and the comparison sample was obtained.
[0062] The following evaluation was performed to these samples.
1. Surface roughness (Ra), concavo-convex average height (H), and concavo-convex average width of face (L) : measure in the AFM (atomic force microscope) mode of a scanning probe microscope (digital INSU vine face company make D3000).
2. Fog resistance : contain for 5 minutes in a refrigerator (about 0 degree C), leave it under 28 degrees C and the ambient atmosphere of 81% of humidity after that, and check surface cloudiness. Initial fog resistance and the fog resistance after one-week exposure are evaluated.
O : -- it does not bloom cloudy at all but is uninfluential also in a reflected image -- **: to which a reflected image fades slightly although there is no O:cloudiness -- x: with the part which blooms cloudy slightly -- four steps of ** which blooms cloudy clearly -- evaluation.
3. Antifouling property : check the dirt adhesion situation after one-week exposure visually.
O : adhesion of dirt is not accepted but maintains an early detergency. O : although dirt has adhered slightly, evaluate in four steps of ** with the part which is uninfluential in use and **:dirt has adhered and a mirror cannot appear easily in which the front face bloomed cloudy with x:dirt.
In addition, exposure of a sample was installed in the mirror lower part in the shower booth of 80cm around for one week, and was performed by repeating bathing of four persons per day. The evaluation result is shown in Table 3.
[0063]
[Table 3]

		Ra (nm)	H (nm)	L (nm)	初期防曇性	暴露後防曇性	暴露後防汚性	耐摩耗性
実施例11	DC反応性スパッタ（シリカ）	0.99	3.12	21.98	◎	◎	◎	−
	EB蒸着（シリカ）	0.83	2.40	18.32	◎	◎	◎	−
	EB蒸着（アルミナ）	0.86	3.99	17.91	◎	◎	◎	−
	比較例 PETフィルム	1.31	凹凸なし		×	×	×	−
実施例12	ケミカルエッチング（フッ酸処理）	0.47	1.92	20.94	◎	◎	◎	−
実施例13	ケミカルエッチング（ケイフッ化水素酸処	4.63	20.82	44.43	◎	◎	◎	−
実施例14	CVD法（酸化スズ）	9.26	33.92	59.36	◎	◎	◎	−
	耐温水試験	異常無し			−	◎	◎	−
	耐アルカリ試験	異常無し			−	◎	◎	−
実施例15	ケミカルエッチング＋シリカゾル	3.06	11.63	24.51	◎	◎	◎	−
実施例16	ケミカルエッチング＋チタニアゾル	4.02	18.11	38.11	◎	◎	◎	−
実施例17	ケミカルエッチング＋チタンアルコキシド	3.25	9.79	64.49	◎	◎	◎	◎
実施例18	真空蒸着（シリカ）＋スパッタ（チタニア）	3.02	12.78	29.99	◎	◎	◎	−
実施例19	スパッタ（チタニア）	8.51	38.19	57.62	−	−	−	−
	スパッタ（チタニア）＋スパッタ（酸化スズ）	2.39	10.43	25.66	◎	◎	◎	−

[0064] As shown in Table 3, fog resistance did not have the comparison sample. On the other hand, all of samples 1-3 showed the good fog resistance after [not both] one-week exposure have [fog resistance] effect in a reflected image the first stage. Moreover, about antifouling property, dirt adheres and, as for the comparison sample, the front face bloomed cloudy. On the other hand, neither of samples 1-3 was accepted, but adhesion of dirt was maintaining the early detergency for it. It has checked that good fog resistance and antifouling property were acquired by covering the inorganic oxide of a silica and an alumina with DC reactivity spatter and EB vacuum evaporationo to a base material, and forming irregularity.

[0065] Example 12: Hydrofluoric acid treatment (chemical etching)
The mirror front face of 20cm angle was chemically etched by fluoric acid, detailed irregularity was formed, and the sample was obtained. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.

[0066] As shown in Table 3, the good fog resistance after [not both] one-week exposure have [fog resistance] effect in a reflected image was shown the first stage. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that good fog resistance and antifouling property were acquired from this by forming irregularity in a front face by hydrofluoric acid treatment.

[0067] Example 13: Processing by the silicofluoric-acid solution (chemical etching)
By processing the mirror of 20cm angle with a silicofluoric-acid solution, detailed irregularity was formed and the sample was obtained. The same evaluation as an example

11 was performed using this sample. The evaluation result is shown in Table 3.
[0068] As shown in Table 3, the good fog resistance after [not both] one-week exposure have [fog resistance] effect in a reflected image was shown the first stage. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that good fog resistance and antifouling property were acquired from this by forming irregularity in a front face by processing by the silicofluoric-acid solution.
[0069] Example 14: CVD method (tin oxide)
With the CVD method, the mirror front face of 20cm angle was coated with the tin oxide, and the sample was obtained. This sample was equally divided into three and the same evaluation as an example 11 was performed using one sheet. Warm water-proof nature and alkali resistance were evaluated using the two remaining sheets. Evaluation of warm water-proof nature was the approach of checking the existence of the abnormalities of an appearance visually after being immersed in 95-degree C warm water for 12 hours, and after alkali-proof evaluation was immersed in NaOH 5% for 12 hours, it was performed by the approach of checking the existence of the abnormalities of an appearance visually. The same evaluation as an example 11 was performed using the sample which evaluated warm water-proof nature and alkali resistance. The evaluation result is shown in Table 3.
[0070] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that the abnormalities by warm water and alkali were not accepted, but there was no effect also in fog resistance and antifouling property. It has checked that fog resistance and antifouling property strong also against warm water and alkali were acquired by carrying out the coat of the tin oxide with a CVD method, and forming irregularity from this.
[0071] Example 15: By processing with the processing silicofluoric-acid solution by the inorganic oxide sol of a concavo-convex front face, the mirror front face in which detailed irregularity was formed was coated with three kinds of sols for what mixed spherical colloidal silica (solid content concentration [of 30 - 31%], particle diameter of 8-11nm), and lithium silicate, and said spherical colloidal silica and said lithium silicate, respectively, and three kinds of samples were obtained. When irregularity was formed in the mirror front face, nebula was accepted slightly, but by coating said three kinds of sols, even if the front face hit light, an interference fringe and nebula were not accepted at all. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.
[0072] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that good fog resistance and antifouling property were acquired by carrying out coat formation with a metallic oxide further, and making irregularity from this, the base material front face which formed irregularity beforehand.
[0073] Example 16: The processing anatase mold titania sol (15% of solid content concentration) by the titanium oxide sol of a concavo-convex front face was diluted with ethanol 15 times, and coating liquid was adjusted. Apply the above-mentioned coating liquid to the mirror front face which formed detailed irregularity by silicofluoric-acid solution processing by the flow coating method, it was made to season naturally, and the

sample was obtained. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.
[0074] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that good fog resistance and antifouling property were acquired by applying a metallic-oxide sol to the base material front face which formed irregularity beforehand further, and forming irregularity in it from this.
[0075] Example 17: The processing titanium alkoxide solution (the Nippon Soda make, NDH510C, 5% of solid content concentration) by the alkoxide of a concavo-convex front face was diluted with ethanol twice, and coating liquid was adjusted. It applied to the mirror front face which formed detailed irregularity for the above-mentioned coating liquid by silicofluoric-acid solution processing by the flow coating method, it calcinated at 500 degrees C for 30 minutes, and the sample was obtained. The same evaluation and wear-resistant evaluation as an example 11 were performed using this sample. Wear-resistant evaluation was performed by the same approach as examples 1-9. The evaluation result is shown in Table 3.
[0076] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. In antifriction evaluation, a blemish did not stick at all. It has checked that wear-resistant good irregularity could be formed in the base material front face which formed irregularity beforehand from this by carrying out coat baking of the metallic oxide further. Moreover, it has also checked that good fog resistance and antifouling property were acquired.
[0077] Example 18: The silica was coated with the spatter processing vacuum evaporation technique of a concavo-convex front face, the mirror front face of 20cm angle which formed irregularity beforehand was further coated with the titania by the spatter, and the sample was obtained. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.
[0078] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that still better fog resistance and antifouling property were acquired from this by giving irregularity to the base material front face which carried out concavo-convex formation with vacuum deposition further.
[0079] Example 19: The titania was coated by spatter processing 2 spatter of a concavo-convex front face, the mirror front face of 20cm angle in which predetermined irregularity was formed was further coated with the tin oxide by the spatter, and the sample was obtained. The same evaluation as an example 11 was performed using this sample. The evaluation result is shown in Table 3.
[0080] As shown in Table 3, the good fog resistance after [not both] the first stage and one-week exposure have [fog resistance] effect in a reflected image was shown. Moreover, dirt did not adhere, either but the early detergency was maintained. It has checked that still better fog resistance and antifouling property were acquired from this by giving irregularity to the base material front face which carried out concavo-convex

formation by the spatter further.
[0081] Example 20: By the related spatter of thickness, and antifog and antifouling property, the mirror front face of 20cm angle was coated with the titania by various thickness, and the sample was obtained. The approach estimated antifog and antifouling property like the example 11 using this sample. It united and appearance evaluation was also performed. The approach is the same as that of examples 1-9. An evaluation result is shown in Table 4.
[0082]
[Table 4]

膜厚	Ra (nm)	H (nm)	L (nm)	外観	初期防曇性	暴露後防曇性	暴露後防汚性
300nm	6.65	27.56	43.79	◎	◎	◎	◎
400nm	7.16	29.14	46.01	◎	◎	◎	◎
500nm	8.51	38.19	57.62	△	◎	◎	◎

[0083] Although there was no difference in antifog and antifouling property by the difference in thickness within the limits of this experiment as shown in Table 4, by 500nm, the interference fringe was seen for thickness, and the exterior had a problem. From this, thickness has checked that 400nm or less was desirable.
[0084] The mirror front face was coated with five kinds of metallic-oxide sols, example 21 alumina sol, a silica sol, a tin-oxide sol, a titania sol, and a zirconia sol, respectively, and the sample was obtained. After measuring surface roughness (Ra), concavo-convex average height (H), the concavo-convex average width of face (L), and the zero charge point of each sample, it installed in the bath interior of a room, and was exposed for two weeks. Bathing made throughout [exposure term] four persons per day, and we decided to perform the intentional water or intentional ** to a mirror plane, no washing, etc. It was exposed by installing a normal mirror similarly for a comparison. In addition, a zero charge point is pH of a water solution in case F-potential is set to 0, and when it puts in into the water solution of pH higher than the value of a zero charge point, when F-potential puts in into the water solution of pH lower than it, it just becomes negative. The zero charge point measurement on the front face of a mirror calculated pH of an electrolyte water solution when an electroendosmose style is measured as a monitor particle of light scattering and an electroendosmose style is set to 0 in polystyrene latex with the titrimetric method using the laser F-potential meter (the product made from the Otsuka electron, ELS-6000). Surface roughness (Ra), concavo-convex average height (H), and concavo-convex average width of face (L) were measured in the AFM (atomic force microscope) mode of a scanning probe microscope (digital INSU vine face company make D3000). The sample was taken out from the bathroom after two-week exposure, and four-step evaluation by viewing was carried out according to the drip nature evaluation approach of examples 1-9. The result is shown in the following table.
[0085]
[Table 5]

試料	Ra (nm)	H (nm)	L (nm)	零電荷点	流滴性評価
アルミナ	4.46	13.94	36.95	7.5	△
シリカ	3.37	10.09	51.02	3.6	◎
酸化スズ	2.79	9.84	24.57	5.4	○
チタニア	0.57	2.46	11.34	6.0	○
ジルコニア	0.18	0.85	9.26	5.5	○
ノーマル鏡	0.05	凹凸なし		3.6	×

[0086] Although the Normal mirror had the zero charge point equivalent to the silica sol mirror as shown in Table 5, the water wetted area was not filled to 60%. On the other hand, in the mirror which applied various sols, the silica mirror showed [the alumina mirror / the tin-oxide zirconia mirror] 100% of water wetted area 80% or more 60% or more. As mentioned above, it has checked that it was hard to maintain a hydrophilic property only with detailed irregularity as the value of a zero charge point was small (F-potential is negative). that is, detailed irregularity and a zero charge point are less than seven (it sets to underwater [of the pH7 neighborhood] and F-potential is negative) -- union ****** -- it has checked that could maintain a good hydrophilic property and fog resistance, antifouling property, waterdrop formation tightness, and waterdrop adhesion tightness were acquired by water screen formation, so that a zero charge point is still lower by things.

[0087] It was immersed in 80-degree C warm water for 24 hours, nature was made to dry example 22 mirror after that, and the sample was obtained. This sample was evaluated like the example 19. Consequently, surface roughness (Ra) was [3.094nm and the concavo-convex average width of face (L) of 0.675nm and concavo-convex average height (H)] 24.899nm. All are O and evaluation of initial fog resistance, after [exposure] fog resistance, and antifouling property has checked that fog resistance and a detergency even with after [good] exposure could be maintained. It has checked that fog resistance and antifouling property also with good also forming irregularity in a base material front face by warm water immersion were acquired from this.

[0088] The example 23200mmx300mm mirror was prepared. The sample which applied the silica sol and formed irregularity was obtained. The silver-nitrate water solution was applied on it after concavo-convex formation by the silica sol, and the sample which carried out photoreduction immobilization of the silver using the BLB lamp was obtained. The sample which fixed direct silver to the mirror front face was also prepared for the comparison. The spore of mold was made to adhere to a front face after measurement, the surface roughness (Ra) of these samples, concavo-convex average height (H), and concavo-convex average width of face (L) were installed in the bath interior of a room, and exposure was performed for two weeks. Bathing of an exposure term throughout took day for four persons per. After two weeks, while checking the generating situation of the dirt adhesion and mold, the same approach as examples 1-9 estimated drip nature. A result is shown in Table 6. In addition, surface roughness (Ra), concavo-convex average height (H), and concavo-convex average width of face (L) were measured in the AFM (atomic force microscope) mode of a scanning probe microscope (digital INSU vine face company make D3000).

[0089]
[Table 6]

	Ra (nm)	H (nm)	L (nm)	滴滴性	カビ発生	汚れ付着
凹凸	2.65	7.97	50.31	△	あり	ほとんどなし
凹凸+銀	2.87	8.12	48.19	○	なし	ほとんどなし
銀	0.32	凹凸なし		×	なし	あり

[0090] As shown in Table 6, although the comparison sample did not generate mold on a front face, dirt had adhered and the antifog effectiveness by less than 60% of water wetted areas and the drip was in a situation which is not acquired. Dirt hardly adhered but the sample which formed irregularity by the silica held drip nature barely with 60% or more of water wetted areas. However, when mold occurred in spots in the front face, the part had lost the hydrophilic property and it was used, it was in the condition which is not desirable. On the other hand, in spite of having been as practically equal as the sample of the point in which, as for what fixed silver on the irregularity of a silica, surface roughness, and concavo-convex average height and width of face formed irregularity by the silica, mold did not adhere, either but, as for the water wetted area, maintained 80% or more and good drip nature. It has checked that generating of the mold on the front face of a member could be prevented, and a hydrophilic property could be maintained good by it by fixing silver on irregularity from this. As mentioned above, it was suggested by combining irregularity and an antibacterial metal that a hydrophilic property can maintain in the condition good for a long period of time.
[0091]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The typical sectional view of a concavo-convex front face is shown.
[Drawing 2] The typical sectional view at the time of covering a metal oxide layer to a base material, and forming irregularity is shown.
[Drawing 3] The typical sectional view at the time of forming direct irregularity is shown in a base material.
[Drawing 4] The typical sectional view at the time of forming irregularity further on a concavo-convex front face is shown.
[Description of Notations]

H: Concavo-convex height
L: Concavo-convex width of face
1: Base material
2: Metal oxide layer

[Translation done.]
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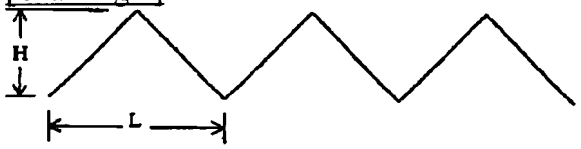
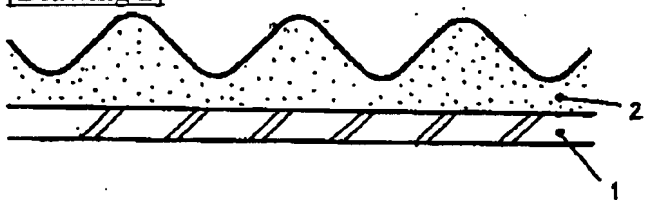
damages caused by the use of this translation.
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

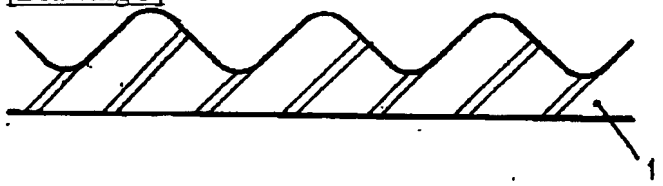
[Drawing 1]



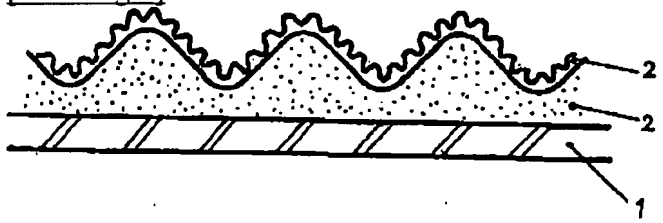
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]